KERNFORSCHUNGSZENTRUM

KARLSRUHE

Juli 1975

KFK 1905/I
EUR 5203 e

Projekt Spaltstoffflußkontrolle

The Interlaboratory Experiment IDA-72 on Mass Spectrometric Isotope Dilution Analysis

Volume I

W. Beyrich, E. Drosselmeyer

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W. Beyrich [x] and E. Drosselmeyer [xx]

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The Interlaboratory Experiment IDA-72
on Mass Spectrometric Isotope Dilution Analysis

Within the framework of the Safeguards Project of the Federal Republic of Germany at the Nuclear Research Center Karlsruhe an analytical intercomparison program was carried out in cooperation with 22 laboratories of 13 countries or international organizations. The main objective was the acquisition of basic data on the errors involved in the mass spectrometric isotope dilution analysis if it is applied to the determination of uranium and plutonium in diluted active feed solutions of reprocessing plants in routine operation. The results were evaluated by statistical methods mainly in regard to the calculation of the estimates of the variances for the different error components contributing to the total error of this analytical technique. Furthermore, the performance of two new methods for sample conditioning suggested by the International Atomic Energy Agency, Vienna, and the European Institute for Transuranium Elements (EURATOM), Karlsruhe, was successfully tested.

The results of some investigations on the stability of diluted high active feed solutions and on comparison analyses by X-ray fluorescence spectrometry are also included.

Data on the analytical efforts (manhours) invested in this study are reported as well as general experiences made in the organization and performance of an experiment on such an extended international level.

Der Interlaboratoriumstest IDA-72 zur massenspektrometrischen Isotopenverdünnungsanalyse

Im Rahmen des Projekts Spaltstoffflußkontrolle der Bundesrepublik Deutschland wurde am Kernforschungszentrum Karlsruhe in Zusammenarbeit mit 22 Laboratorien aus 13 Ländern oder internationalen Organisationen ein analytisches Vergleichsprogramm durchgeführt. Das Hauptziel dieser Untersuchungen war die Gewinnung von Daten über die Fehler, mit denen die massenspektrometrische Isotopenverdünnungsanalyse behaftet ist, wenn sie im Routinebetrieb zur Uran- und Plutoniumbestimmung in verdünnten, aktiven Eingangslösungen von Wiederaufarbeitungsanlagen angewendet wird. Die Ergebnisse wurden statistisch ausgewertet, insbesondere hinsichtlich der Schätzwerte für die verschiedenen Fehlerkomponenten, die zum Gesamtfehler dieser Analysentechnik beitragen. Darüberhinaus wurde die Leistungsfähigkeit zweier neuer Methoden zur Probenbehandlung erfolgreich geprüft, die von der Internationalen Atomenergiebehörde, Wien, und dem Europäischen Institut für Transurane (EURATOM), Karlsruhe, vorgeschlagen worden waren.

Die Ergebnisse einiger Untersuchungen über die Stabilität verdünnter, aktiver Eingangslösungen und röntgenfluoreszenzspektrometrische Vergleichsanalysen sind ebenfalls eingeschlossen.

Weiterhin werden Daten über den analytischen Aufwand (Mannstunden) dieser Studien aufgeführt sowie allgemeine Erfahrungen, die bei der Organisation und Durchführung des Experimentes auf einer so ausgedehnten internationalen Ebene gemacht wurden.

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Preface

The first series of interlaboratory tests for a number of measurement methods relevant to safeguards, in the framework of the safeguards project, Federal Republic of Germany, was carried out during the years 1970-71. One of the methods tested was the mass spectrometric isotope dilution analysis for the concentration determination of U and Pu in active solutions from the input tank of a fuel reprocessing plant. Since the test could be carried out with only a limited number of laboratories, it was planned as a preliminary study on which more elaborated investigations could be based.

In a meeting held in December 1971 at the International Atomic Energy Agency, Vienna, in which about 14 organizations and laboratories were represented, the necessity of repeating the interlabtest on Isotopic Dilution Analysis (IDA) was emphasized. The test was to be carried out under well defined conditions and with the participation of a large number of laboratories (the number suggested was between 10-20) so that statistically significant results could be obtained. Out of the deliberations of this meeting the idea of the interlabtest "IDA-72" was born.

The participants at the meeting recommended that some additional interlab experiments be carried out in the frame of IDA-72 to investigate a number of other related problems (e.g. stability of the active sample as a function of time and acidity, errors associated with different types of spiking techniques etc.).

It was also agreed upon at that meeting that the Safeguards Project Karlsruhe would take over the responsibility for coordination, evaluation and overall organization of the whole experiment. All the investigations in connection with this experiment would be carried out by the participating laboratories on a voluntary basis.

The response to this experiment was beyond all expectations. Finally 22 wellknown laboratories from 13 countries and international organizations took part in the IDA-72 test. A list of the participating laboratories is given below. It was a spontaneous expression of the importance which such laboratories attached to this type of experiments.

From the point of view of safeguards the importance and necessity of such experiments cannot be overemphasized. Only in this manner can the major components of errors in a measurement method under routine operating conditions be established. Since the present day international safeguards of nuclear materials is mainly based on the concept of measured material balance, dependable data on these error components are essential for making a safeguards relevant statement on the socalled "Material Unaccounted For (MUF)" in a nuclear facility. Particularly for this reason the safeguards organizations EURATOM and the IAEA were actively involved in this experiment.

The IDA-72 experiment could not be brought to a successful conclusion without the excellent spirit of cooperation shown by all the participating organizations. The work load expanded considerably during the course of this experiment. Considering the fact that all their services were offered on a voluntary basis special thanks are due to them.

In particular we would like to express our appreciation of the assistance given and work carried out by the following organizations which took care for the preparation of the many different samples:

CBNM - Central Bureau for Nuclear Measurements (EURATOM), Geel, Belgium

EUROCHEMIC - European Company for Chemical Processing of Irradiated Fuels, Analytical Laboratory, Mol, Belgium

IAEA - International Atomic Energy Agency, Vienna, Austria

TU - European Institute for Transuranium Elements (EURATOM), Karlsruhe, Germany

The whole responsibility of coordination, organization and evaluation of this experiment lay on the capable shoulders of Dr. W. Beyrich and Dr. Elisabeth Drosselmeyer both of whom had kindly agreed to offer their services to the project for this work. During almost 3 1/2 years of intensive work quite a number of unforeseen problems had to be solved, new evaluation methods had to be developed, new forms of organizations had to be worked out in connection with this fairly large and complex international venture. I would like to take this opportunity to express my appreciation of the efficient manner in which they have handled this job.

IDA-72 which was several orders of magnitude larger and complexer than the previous interlabtests carried out by the project, demonstrated once again the feasibility of investigating difficult technical and scientific problems on an international scale.

D. Gupta
Head, Safeguards Project
Federal Republic of Germany

Acknowledgement

This paper reports on the results of the combined efforts of the numerous participants of the laboratories listed below. To all these the authors would like to express their special thanks for the valuable and pleasant cooperation. In addition the interest in and support of this experiment by the project leaders of the Karlsruhe Safeguards Project Dr. Dipak Gupta and Professor Dr. Wolf Häfele is gratefully acknowledged.

The authors also appreciate the diligent and kind assistance of Jürgen Henkenhaf, Monika Mäule, Dieter Nentwich, Hans-Eberhard Otto, Edith Wortmann and Hannelore Zinecker in the general organization of the experiment and specially in the preparation of sample transport, data handling, typing and correction of the manuscripts and preparing the drawings.

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1. Introduction

The analytical intercomparison experiments initiated during the last years by the Safeguards Project of the Federal Republic of Germany and executed in close cooperation with many laboratories of different nations had the main goal to explore the present state of the art of specific analytical methods when they are used for safeguards purposes under routine conditions. This objective is different from the aims of other intercomparison programs in this field /Ref. 1 and 2/ and necessitates some specific features of the experimental layout in order to obtain results which reflect the conditions of practice as realisticly as possible:

- Firstly, the sample material has to be taken from actual industrial processes in order to be of representative composition including all possible impurities. The exact composition of such material is necessarily unknown.

- Secondly, the laboratories participating in such an experiment have to perform the analyses under routine conditions and may not invest extraordinary efforts. As a consequence of this, also less satisfactory data have to be reported. This can only be expected if the evaluation group does not belong to an organization with any control function in safeguards and, furthermore, if it can be guaranteed that the results are published in a codified manner only.

- Thirdly, a sufficiently high number of laboratories has to participate in the test in order to allow a meaningful statistical evaluation and to obtain representative results.

The experimental structure of these "interlaboratory tests" is basicly the same in all cases:

A certain, homogeneous sample material is distributed among the participating laboratories, all these laboratories analyse this material with the same number of repetitions in the various steps of the procedure and, finally, the results obtained are evaluated by statistical methods.

The aim of this evaluation is mainly to estimate the total error of the method under investigation and to subdivide it into components which can be attributed to specific steps of the analytical procedure.

From the safeguards point of view, the particular interest in the capability of the mass spectrometric isotope dilution analysis investigated in the experiment IDA-72 is caused by the fact that the very important data on the amounts of uranium and plutonium present in the solutions of dissolved spent fuel elements are gained by this analytical procedure, and this is one of the most critical steps in fuel cycle control.

In this analytical method a known amount of the sample solution is blended with a known amount of an indicator isotope (the "spike") of the element to be determined. From the ratio indicator isotope/sample isotope - generally the mass isotope of the element in the sample - and the masses of the spike and sample solution aliquots the concentration of the sample isotope can be calculated /Par. 3.5.1/. Some corrections have to be applied if - as usual - the composition of the element under investigation is not monoisotopic in the sample and/or the spike solution and if not the concentration of a specific isotope but that of the total element is asked. It is the outstanding feature of the isotope dilution analysis that exclusively mass spectrometric determinations of isotopic ratios and weighings are required - both being analytical procedures which can be performed with very high accuracy.

Preliminary studies on this subject were already made in 1970 in the framework of the joint integral safeguards experiment "JEX-70" /3/[1]. Starting from these results, the general outlines for the experiment IDA-72 were elaborated by a group of experts which met in December 1971 at Vienna around some representatives of those laboratories which had already participated in JEX-70.

It was decided that the experiment should be carried out during 1972 and that it should consist of a standard part, obligatory for all participants, and some additional parts, for which voluntary participation of those laboratories, which would be interested and able to invest more time and money, would be asked.

The "standard experiment" should be concerned with the separation and estimation of the error components contributing to the total error in the uranium and plutonium concentration determinations performed by mass spectrometric isotope dilution analysis on diluted active feed solutions and synthetic reference solutions without fission products.

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[1] This experiment is also called "Mol III" with reference to the EUROCHEMIC reprocessing plant in Mol, Belgium, where the main part of the experimental work was carried out.

The "additional experiments" should be directed to the following particular subjects:

- errors involved in the spiking procedure ("self spike experiment")
- testing of new methods of sample conditioning proposed by the International Atomic Energy Agency ("dry spike experiment") and the European Institute for Transuranium Elements, EURATOM ("aluminium capsule experiments")
- stability of diluted active feed solutions in dependence on acidity, plutonium concentration and the presence of fission products ("aging experiments") and
- comparison of the uranium and plutonium concentrations with results obtained by X-ray fluorescence spectrometry.

Concerning the methods of sample preparation and mass spectrometric measurement it was recommended that each laboratory should use its standard procedures in order to avoid additional error contributions due to unfamiliar sample handling. For the same reason, no recommendations were given in respect to the use of mass spectrometry or α-spectrometry for the determination of the isotope Pu-238.

The European Company for Chemical Processing of Irradiated Fuels (EUROCHEMIC), in Mol, Belgium offered to provide the necessary active sample material, the Central Bureau for Nuclear Measurements (CBNM) of EURATOM in Geel, Belgium agreed to prepare all necessary spike and reference solutions.

The Institutt for Atomenergi at Kjeller, Norway, the Joint Research Center of EURATOM at Ispra, Italy, and the Los Alamos Scientific Laboratory at Los Alamos, USA were ready to take over the excessively high efforts of the aging experiments.

In total 22 laboratories of 13 countries or international organizations notified their interest to participate, most of them not only in the standard part but also in one or more of the additional experiments1).

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1)As two laboratories cooperated in the performance of the analyses, one was unable to supply the results in time and one could only contribute to the sample preparation, the measurements of 19 laboratories were finally available for the evaluation of the standard experiment.

As it can be seen from the data, the participants gave on their analytical and data reporting efforts for the experiment, on average each laboratory has worked about 7 man weeks on the standard experiment and 9 man weeks in cases where also additional experimental work was included. The efforts of those laboratories working in the aging experiments were considerably higher.

After completion of the measurements and their preliminary evaluation in February 1974 a final meeting was held at Karlsruhe for a detailed discussion of the experimental results by the experts of the participating laboratories. The minutes of this meeting are enclosed in Par. 8 of this report as the deliberations of this conference, are the basis of the conclusions and recommendations summarized at the end of this paper.

2. Performance of the Experiment

2.1 Survey of the Experimental Design

A simplified scheme of the layout of the standard experiment is given in Fig. 2-1.

Two active sample solutions named "A" and "B" of slightly different concentrations in the order of 1 mg uranium/g solution and 10 µg plutonium/g solution were obtained by dilution of active feed solution samples, taken at EUROCHEMIC, with 5 M nitric acid in a well known ratio.
In order to avoid any possible influence of sample instability on the analytical results of the individual laboratories, half of each of these solutions was spiked in total within 12 hours after sampling with an U-233/Pu-242 mixed spike solution prepared by the CBNM. The same was done with a synthetic reference solution "R" of similar and well known composition which had also been prepared by this institute.

Besides samples of these spiked solutions, each laboratory obtained samples of the unspiked solutions A, B and R. Instead of mixed spike solution, samples of the single U-233 and Pu-242 spike solution components were distributed in order to avoid reseparation of the mixture for mass spectrometric determination of their isotopic composition.

The analytical procedures followed by the laboratories on the different sample solutions are discussed in Par. 3.1. Only the treatment of the spiked **samples** - the most essential part of the isotope dilution analyses - is indicated in Fig. 2-1: Chemical sample preparation of each of these solutions was done in triplicate followed by mass spectrometric measurement of one filament loading with 10 scans of the isotopic ratios.

Because of the use of the same spike solution for the three sample solutions A, B and R and because all the spiked samples for the various laboratories were obtained by one single aliquotation per type of sample

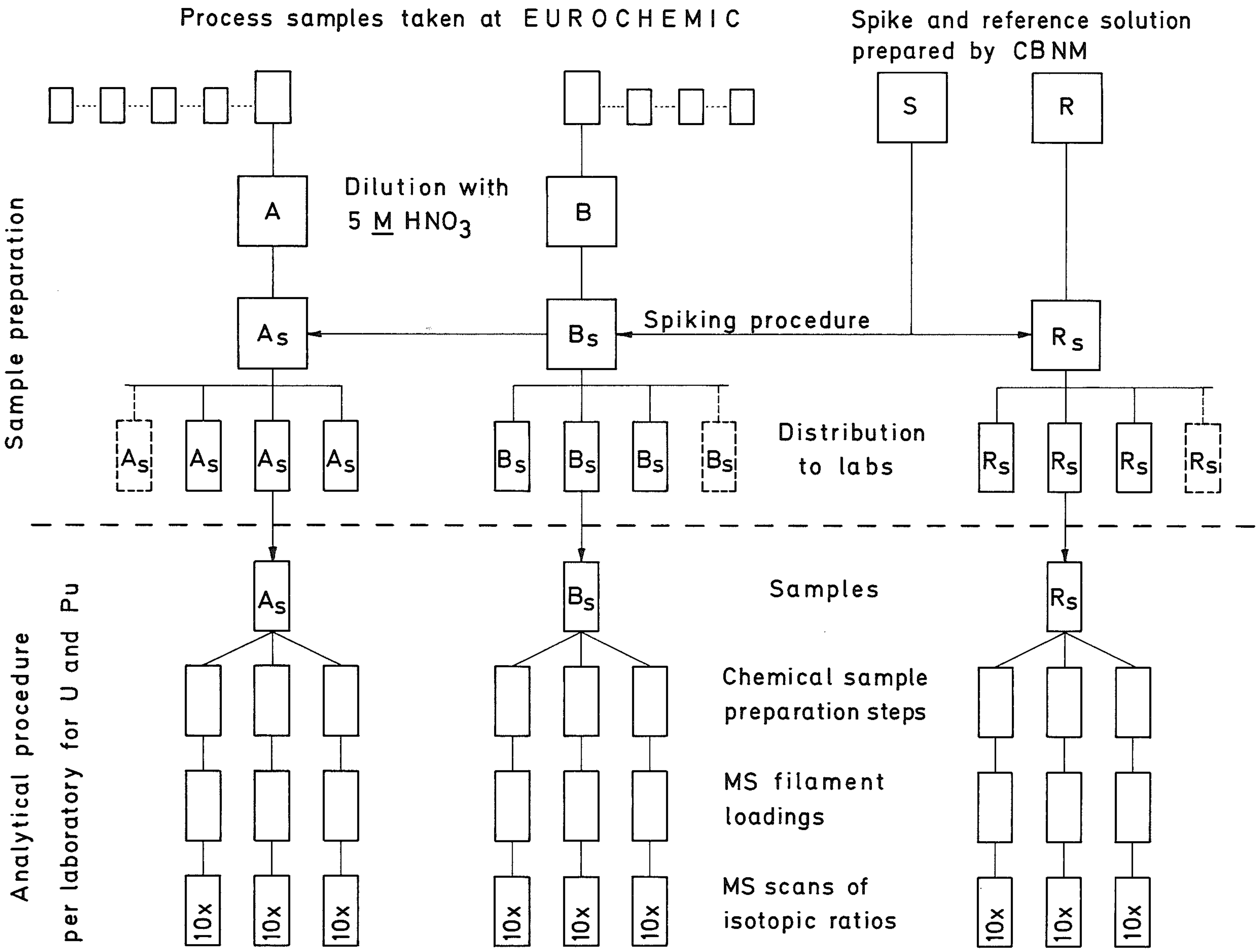


Fig. 2-1 IDA-72: Simplified Scheme of Standard Experiment

(Distribution and measurement of spike and unspiked sample solution not considered) solution (A,B,R) any errors in the calibration of the spike solution or during aliquotation would only bias all the measurements in total or at least all measurements of the same sample solution, respectively. However, no information on the contribution of the spiking procedure to the statistical error can be gained from the evaluation of this standard experiment.

For this reason, the so-called self spike experiment was performed. In this additional study, a number of laboratories spiked and analyzed the R-solution in triplicate, using their own spike solution. The synthetical R-solution was used for this test because it was considered as more stable during the time of storage and transportation to the individual laboratories than the active A- und B-solutions, containing fission products. In order to detect eventual loss of sample material by evaporation, the weight of the sample bottles before and after shipment was carefully checked.

As the spiking error should mainly be caused by errors in spike solution calibration and/or aliquotation it was considered to be independent on the type of sample solution.

As mentioned above /Par. 1/, also the capability of two new methods for sample treatment proposed by the International Atomic Energy Agency (IAEA) and the European Institute for Transuranium Elements (TU) should be tested in the additional dry spike- and aluminium capsule experiments, respectively.

The IAEA method described in Vol. II, Chapt. 4 can be summarized as follows: Instead of mixing spike and sample solutions in the liquid phase, first the aliquot of the pure spike solution is given in a small sample container and evaporated to dryness and, subsequently, the aliquot of the sample solution is added and also evaporated to dryness. A normal glass vial is used and the dried material is recovered from the glass surface for analysis with nitric acid.

Therefore, by the dry spike experiment, it had to be demonstrated that the isotopic composition of the solution obtained by redissolving the sample and spike material from the surface of the glass vial quantitatively represents the value expected for the mixture of the corresponding aliquots.

Also the procedure recommended by the TU, which is described in Vol. II, Chapt. 5, follows the basic principal of evaporating sample and spike aliquots to dryness. However, as thin aluminium-cpasules are used instead of glass vials, by complete dissolution of these small containers, the evaporated aliquot can be recovered quantitatively.

In order to check also this additional feature of the aluminium capsule technique, in this case splitting of the performance test into two parts became necessary:

Layout and scope of part I was made identical with that of the dry spike experiment by evaporating spike and sample aliquots within the same capsule. In part II of this study, however, different capsules were used for the evaporation of spike and sample aliquots. They had to be dissolved quantitatively in order to obtain solutions of defined concentrations which, afterwards, could be used to prepare a spiked solution in the liquid phase as usual. The structure of these experiments is shown in Fig. 5-1 and 5-6 below.

In order to meet the conditions of practice as close as possible, it was decided to use active A-sample solution for these investigations and to check the performance of these techniques by comparison of the concentration determinations with the corresponding values obtained in the standard experiment. It has to be noted, however, that the structure of these tests and the standard experiment are not completely identical as - different to the standard experiment - individual aliquotation was required for each sample bottle.

The aging experiment was split into three parts executed in different laboratories. The aim was to study the possible influence of the following parameters on the aging behaviour of Pu-containing solutions:

I Molarity of the solution:

The values $8\underline{M}$, $5\underline{M}$, $2.5\underline{M}$ were chosen for the nitric acidity. Active feed solution was taken with a Pu concentration of about 10 µg/ml solution as in the standard experiment. The time interval, in which the solutions were studied, was 5.5 months.

II Pu concentration of the solution:

The values 2, 10 and 20 µg Pu/ml solution were chosen. The molarity was 5M in these cases as in the standard experiment. The time interval under study was 4.5 months, and the material was again a dilution from active feed material.

III Absence of fission products;
aging effects in the short time range.

In this case a special study was executed on possible aging effects in the time interval from 2 to 10 days. The study was done in parallel on the normal active feed solution A and on the synthetic reference solution R, which were both used also in the standard experiment.

In order to define the concentration values at "zero time" for reference, one sample of each solution was spiked immediately after its preparation at CBNM. Furthermore, besides the unspiked sample solutions, samples of the mixed spike solution used by CBNM were shipped to the three laboratories for the further analyses.

The X-ray-fluorescence method was applied in order to compare the U- and Pu-concentration values from this determination with the results of the isotope dilution analysis. Undiluted samples of the active feed solution were needed for these measurements, as the plutonium concentration of the A and B solution of the standard experiment was insufficient for a meaningful application of this analytical technique. Comparison of the results consequently requires exact knowledge of the dilution ratios used in preparing the A and B solutions.

2.2 Sampling and Sample Preparation

As already indicated in the introduction, all active sample material for the IDA-experiment was taken and prepared at the EUROCHEMIC reprocessing plant in Mol, Belgium, whereas the CBNM of EURATOM in Geel, Belgium, prepared the spike and reference solutions and performed all necessary aliquotations. The procedures followed are described in detail in Vol. II, Chapter 2 and Chapter 3, respectively.

In the following, only a short survey on these extensive and important parts of the experiment shall be given.

A sketch of the sampling procedures at EUROCHEMIC is shown in Fig. 2-2. On 21st of June, 1972, the samples were taken from a dissolution of TRINO-fuel elements. The burn-up in this pressurized water reactor was estimated to be 21 400 MWd/t, the initial enrichment was 3.897 wt% U-235.

Eight single samples from the series of normal process samples (each 3ml) were used for the IDA experiment. They were taken in the order

$$C, B, A, E_1, E_2, E_3, E_4, F$$

and prepared for the different parts of the experiment by dilution with 5 $\underline{M}$ HNO_3 as indicated in the figure.

The homogeneity of the tank solution was established by density measurements on some of these samples, namely A, B, C and F. The values were consistent.

Aliquots could be filled directly from the densitometer into preweighed aliquot containers, specially designed with the purpose of directly delivering the aliquot to the dilution vessel.

Prior to the dilution step the aliquots are weighed on an analytical balance. With precise density and weight determinations the respective volumes are known precisely.

As the first of all of these samples the undiluted E-samples for x-ray fluorescense measurements were prepared for speedy transportation to the laboratory because of the possible instability of this high active and concentrated material.

The sample solutions A and B had partly to be distributed, partly to be spiked and then distributed as described below. From the C solution (≈ 20 μg Pu/ml) a part called D was separated as starting material for the samples of aging experiment I: By mixing with nitric acid of different acidity, the required sample solutions of 2.5 M, 5 M and 8 M could be obtained, each one with a plutonium concentration of about 10 μg/ml. The C solution (again ≈20 μg Pu/ml) was partly further diluted with 5 M HNO_3 to get solutions with 2 μg Pu/ml, 10 μg Pu/ml and 20 μg Pu/ml for aging experiment II.

A survey on the procedures performed at the CBNM is given in Fig. 2-3. It was the task of this laboratory to prepare five different types of solutions for the standard experiment, namely

- the reference solution R
- the mixed spike solution S
- the spiked reference solution R_s
- the spiked active feed solution A_s and
- the spiked active feed solution B_s .

As the R-solution should have similar concentration and acidity as the active feed solutions A and B, the required characteristics were ≈1 mg U and ≈10 μg Pu per ml of a 5M nitric acid solution. It was obtained by mixing weighed fractions of a uranium reference solution and a plutonium reference solution, prepared from chemically well-characterized NBS materials (U standard: 950 a, Pu standard: 949 c). In respect to the isotopic compositions, there was only little similarity of the synthetic R solution with the diluted active feed solutions A and B. This type of solution has also been used for the self spike experiment and the aging experiment III.

The mixed spike solution S was prepared by blending weighed fractions of chemically and isotopically well defined U-233 and Pu-242 single spike solutions - both nearly monoisotopic and with an element concentration in the order of 1 mg/ml. In order to obtain in the mixed spike solution a Pu/U-concentration ratio similar to that in the solutions

Fig. 2-2 IDA-72: Sampling Procedure and Preparation of Active Feed Solutions at EUROCHEMIC

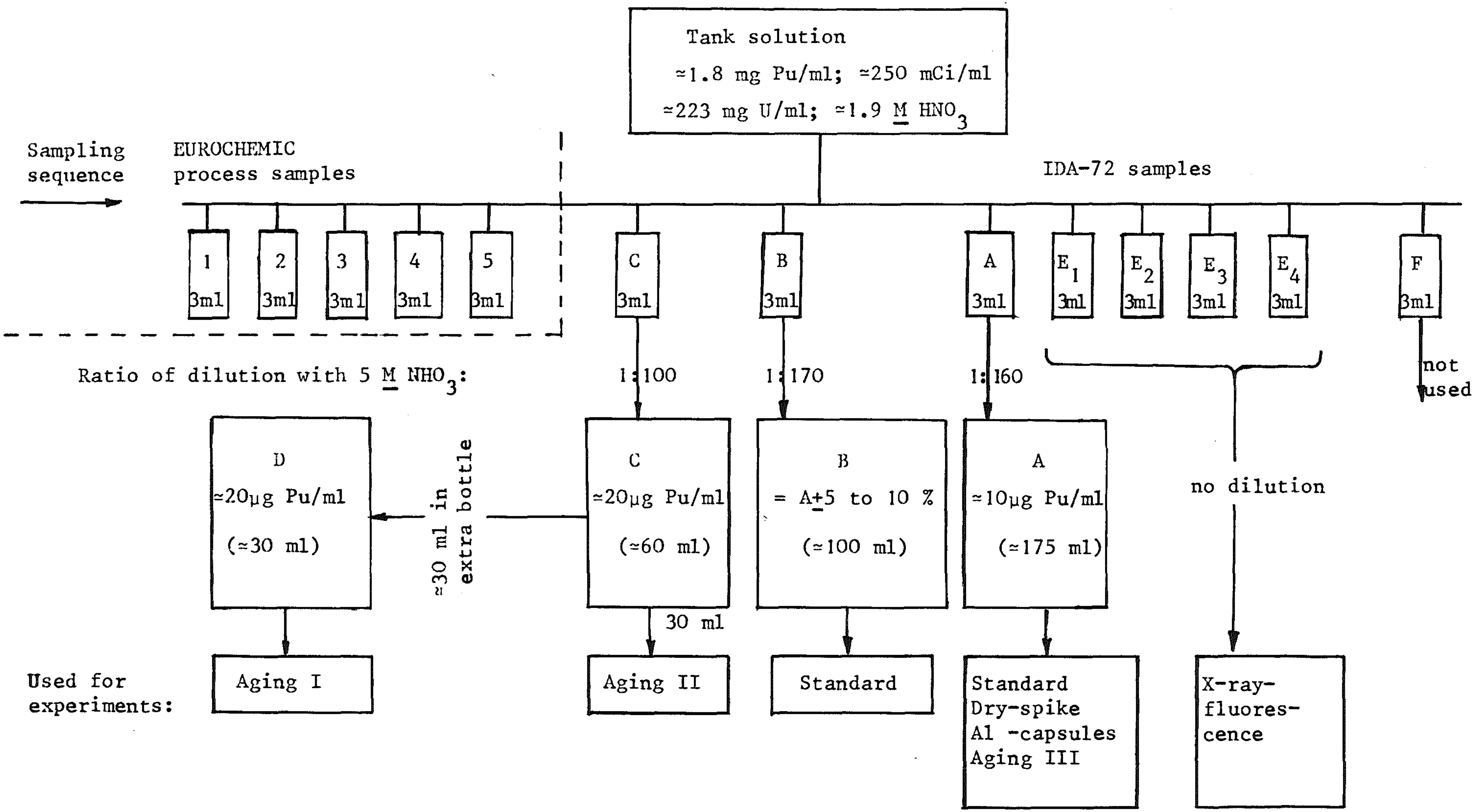
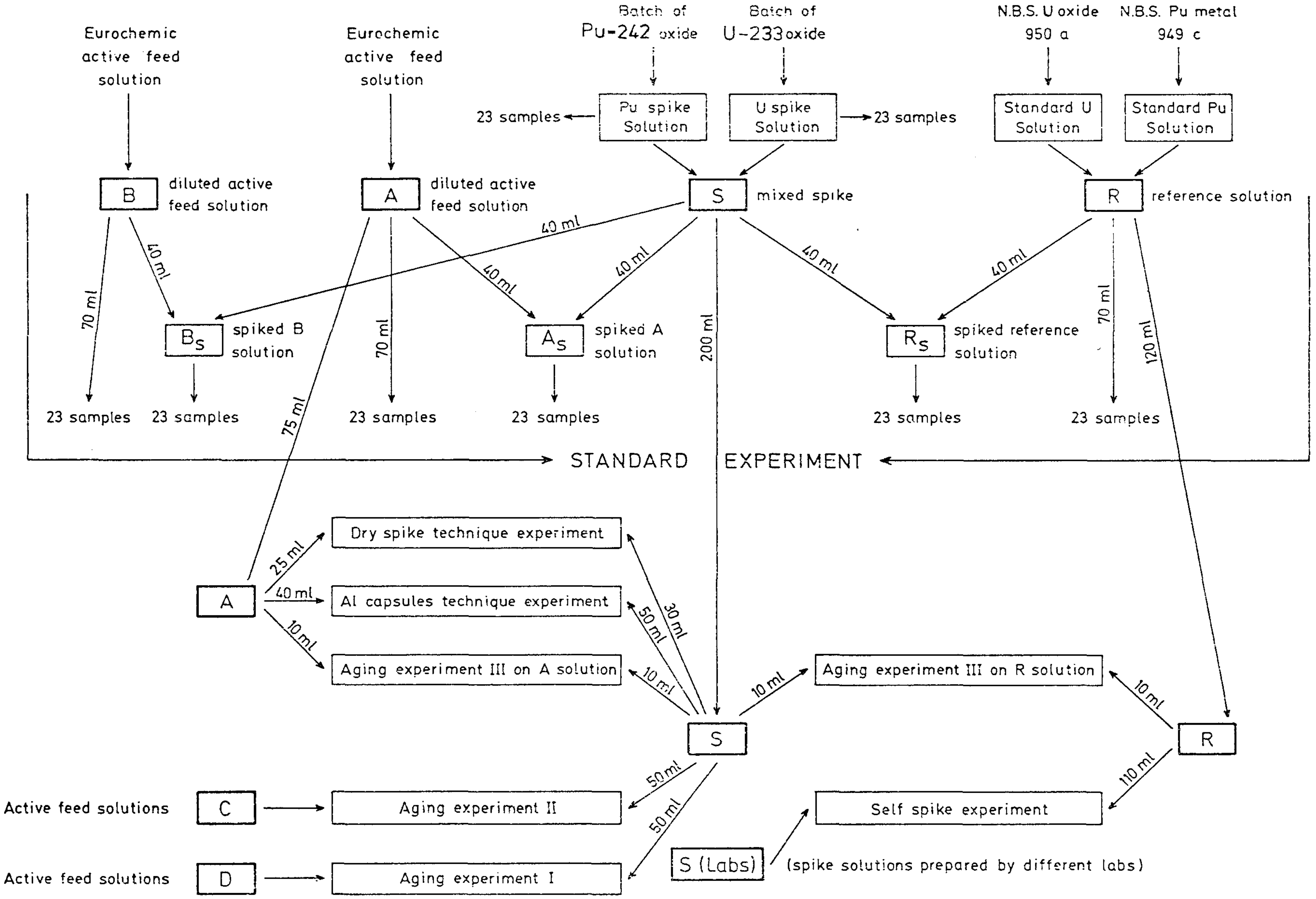


Fig. 2-3 IDA-72 Sample Prepartion at CBNM (EURATOM)



This figure is taken from Volume II, Chapter 3 which had to be analysed, the fraction from the U-233 single spike solution had to be more than 50 times higher by weight than that from the Pu-242 single spike solution.

The use of this mixed spike solution for preparing the spiked sample solutions R_s, A_s and B_s required for the different parts of the experiment is also indicated in Fig. 2-3.

The spiked sample solutions for the standard and aging experiments were stabilized by heating with hydroxylamine for about 45 min. at 70°C.

Concerning the exact aliquotation data of the spiked solutions used in the standard experiment, reference is made to Table 3-17. The values for the spiked samples of the aging experiment are given in Vol. II, Par. 3.3.5 to 3.3.7.

For the standard experiment, also the distribution of the sample materials on the numerous glass vials for shipment to the individual laboratories is shown in Fig. 2-3. The U-233 and Pu-242 single spike solutions were diluted to about 20 µg/ml uranium and plutonium, respectively, before they were bottled in the vials.

Also the samples for the dry spike and aluminium capsule experiments were prepared in the laboratories of the CBNM by members of the IAEA/Vienna and of the EURATOM Transuranium Institute/Karlsruhe.The single steps of these procedures are described in Vol. II, Chapters 4 and 5, the aliquot weights of these individually prepared samples are given in the context of the evaluation of these experiments in Par. 5.

In total, about 300 sample vials and aluminium capsules were prepared for distribution to the participating laboratories.

The best known data on the compositions of the basic solutions used in the IDA experiment are summarized in Table 2-1.

Table 2-1: IDA-72: Composition of Basic Solutions Used

Sample solution	Concentration		Isotopic Composition [atom %]										Reference
	Uranium element: [mg/g sol.] isotope1): [atoms/g sol.]	Plutonium element: [μg/g sol.] isotope1): [atoms/g sol.]	Uranium					Plutonium					
			U-233	U-234	U-235	U-236	U-238	Pu-238	Pu-239	Pu-240	Pu-241	Pu-242	
Diluted active feed solution A	U: 1.1876 U-238: 2.928×10^{18}	Pu: 9.473 Pu-239: 1.707×10^{16}	-	0.0174	2.167	0.3828	97.434	1.059	71.650	16.531	9.121	1.639	Evaluation IDA-experiment Par. 3.4 and Par. 3.5.6
Diluted active feed solution B	U: 1.1324 U-238: 2.792×10^{18}	Pu: 9.023 Pu-239: 1.627×10^{16}	-	0.0167	2.164	0.3829	97.439	1.050	71.696	16.497	9.112	1.646	
Synthetic reference solution R	U: 1.1088 U-238: 2.785×10^{18}	Pu: 8.599 Pu-239: 2.109×10^{16}	-	0.0055	0.7203	-	99.274	0.0039	97.3553	2.5652	0.0724	0.0032	CBNM; Vol. II,Par.3.2.1
Diluted U-233 single spike solution	not measured	not measured	97.779	0.018	0.040	0.003	2.163	-	-	-	-	-	CBNM; Vol. II, Par.3.2.2
Diluted Pu-242 single spike solution	not measured	not measured	-	-	-	-	-	0.003	0.020	0.084	0.075	99.818	
U-233/Pu-242 mixed spike solution S	U: 0.8290 U-233: 2.0931×10^{18}	Pu: 10.085 Pu-242: 2.4594×10^{16}	97.779	0.018	0.040	0.003	2.163	0.0044	1.3084	0.5923	0.1007	97.9942	

Note: The difference in the plutonium isotopic composition of the Pu-242 single spike solution and the U-233/Pu-242 mixed spike solution S is caused by a small plutonium impurity in the U-233 single spike solution.

1) Calculated using for the atomic masses and Avogadro's number the figures given in Vol. II, Chapter 1.

2.3 Packing and Transportation

The preparation for packing and transportation had been done at Karlsruhe. The TRANSNUKLEAR Company at Hanau / Germany was charged with the actual transport to the 13 different countries.

As mentioned before /Par. 2.2/, the samples of active feed solution for analysis by X-ray fluorescence spectrometry had to remain undiluted and therefore required fast transportation to the laboratory at Karlsruhe. In spite of considerable organizational efforts, they left the EUROCHEMIC plant by truck not before June 23, 1972, i.e. two days after sampling. These undiluted sample solutions were left in the original EUROCHEMIC sample vials, which are shown in Fig. 2-4 together with the plastic cartridges in which they are packed. All further containers necessary to meet safety regulations for shipment of these high active samples were supplied by TRANSNUKLEAR.

The glass vials used for all other liquid samples and those for the dry spike experiment are of the SOVIREL[1)] type shown in Fig. 2-5. In order to reduce the risk of loosening of the screw caps during shipment (e.g. by vibration in air transportation), the bottle threads were covered with thin TEFLON-tape which generated a close contact between the glass vial and the plastic screw cap. Furthermore, the plastic caps were fixed by TESA-tape winded around.

Some of the vials had to be checked for possible evaporation losses of sample solution by precise weight determination before shipment and after arrival at the laboratories (R-sample solution for the self spike experiment as well as mixed spike and sample solution for the aging experiments). In these cases difficulties caused by the use of sticking tape had to be expected.

[1)] Tube à vis bouchés No. 461 151 manufactured by SOVIREL, Paris, France.

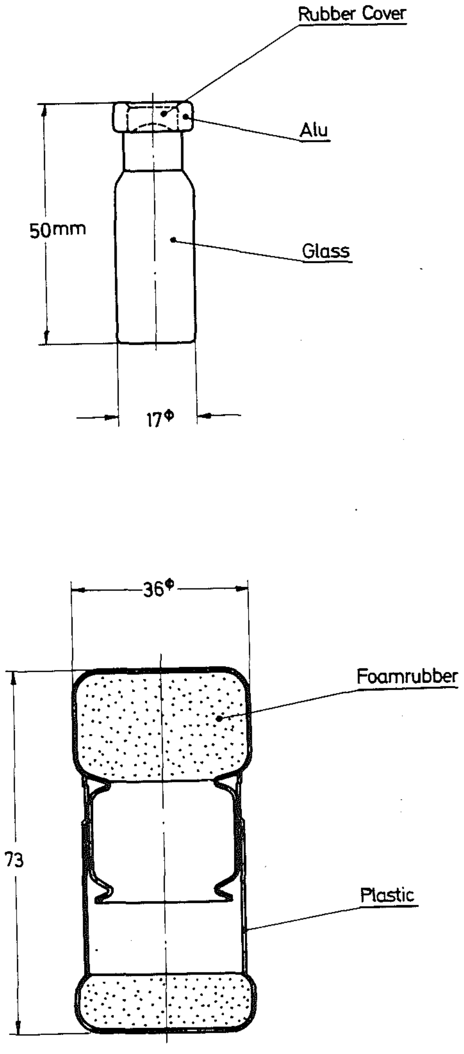


Fig. 2-4 IDA-72: EUROCHEMIC Sample Vial and Plastic Cartridge

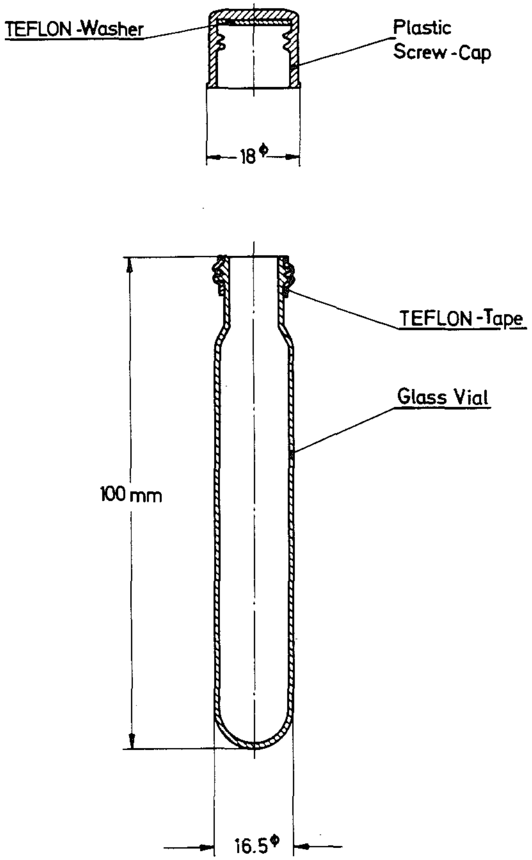


Fig. 2-5 IDA-72: Sovirel Sample Vial

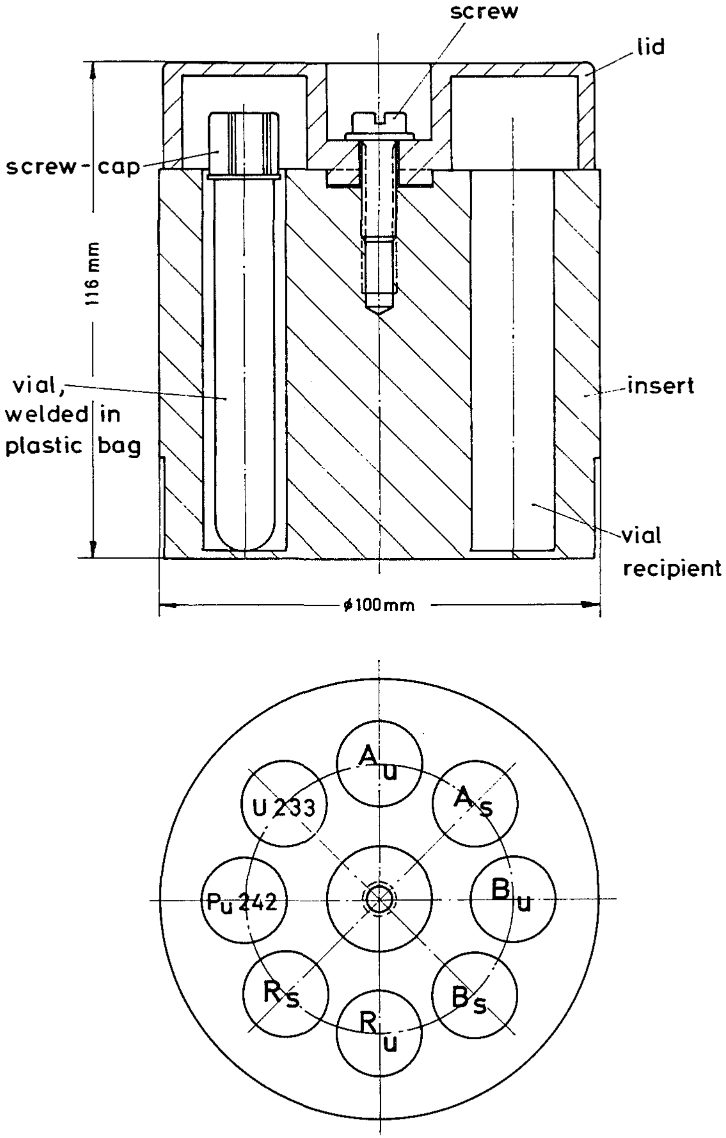


Fig. 2-6 IDA-72: Schematic View of Plastic Insert for Standard Experiment

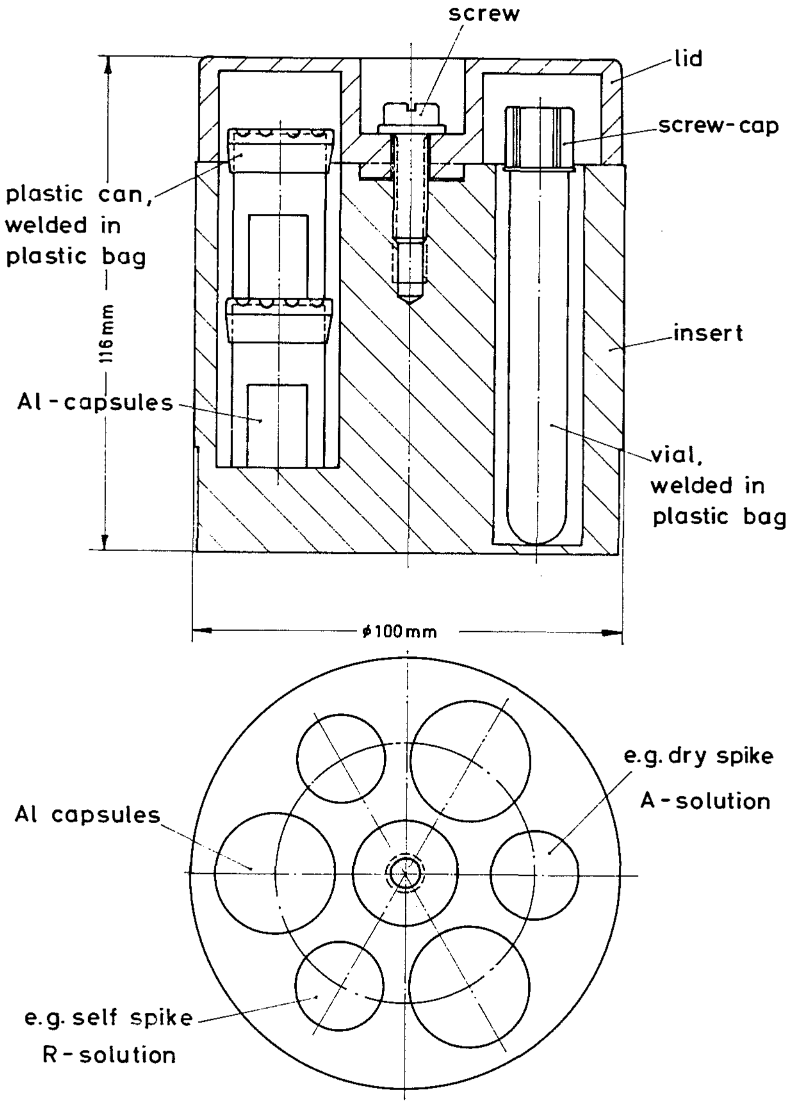


Fig. 2-7 IDA-72: Schematic View of Plastic Insert for Additional Experiments

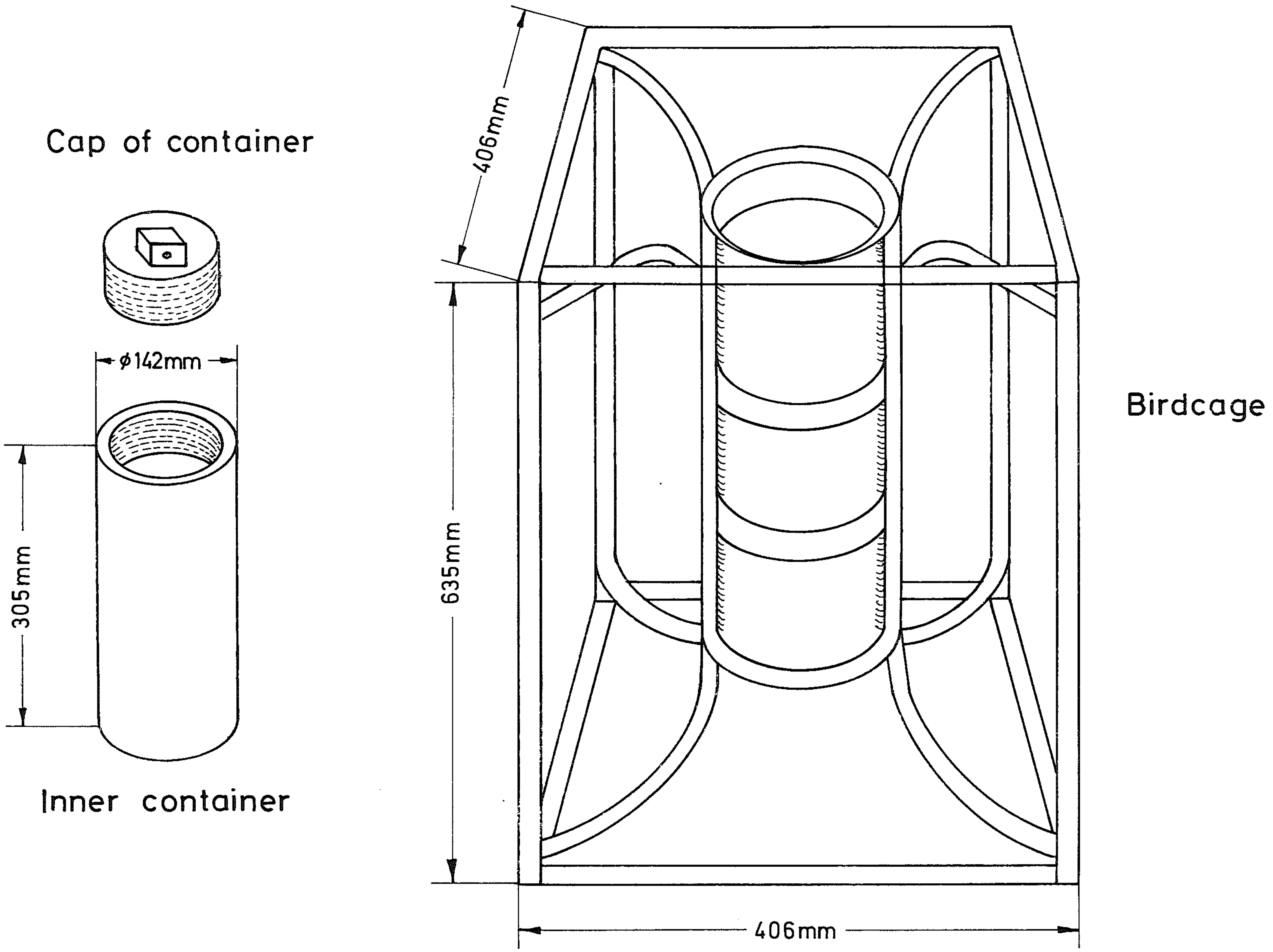


Fig. 2-8 IDA-72: Sketch of LD-1 Birdcage and Inner Container

Furthermore, preceding tests had shown that precise weighings of vials closed with their cap were disturbed by electrostatic charges on this plastic material.

In order to avoid such effects it was therefore intended to close the glass tubes of the vials which required weight determination with small plastic stoppers and to weigh them in this condition without screw caps. In some cases,however, also this method became troublesome,because it was not possible to get the glass tubes firmly closed with the plastic stoppers because of too large variations in their inner diameters.

The aluminium capsules were put in small plastic cans with caps. Each of these cans as well as each of the SOVIREL vials were welded separately in polyethylene bags and then put into plastic inserts as shown in Fig.2-6 and Fig. 2-7, which again were welded in plastic bags. These inserts were prepared at Karlsruhe and fitted into the inner container of the LLD-1 birdcage shown in Fig. 2-8. These birdcages - packed into wooden boxes - were used for transportation as they could be made available at the Research Center Karlsruhe without additional costs.

Although shipment of the samples was prepared in cooperation with TRANSNUKLEAR already since 15 weeks before the sampling date, the transports left the EUROCHEMIC plant in general only 4 to 8 weeks afterwards or even later. The main reason for these long delays are the complicated and extensive administrative regulations being different for each country. The possibility to ensure punctual shipment by early application for the permissions is restricted because of the detailed technical information on sample composition and activity required but not available much in advance.

In total 25 birdcages had to be shipped. After unpacking, one laboratory reported that vials showed **signs** that the solution had leaked out /Par. 8.3.6 /. The outer containment was considered as satisfactory in all cases and no contamination problems were observed.

2.4 Instruments and Measurement Techniques Used by the Laboratories

According to the general outlines elaborated in the conference at Vienna / Par. 1 / the participating laboratories had been invited to use their own methods for the analyses. A questionnaire was distributed in which some information on the used instruments and techniques was requested.

A detailed study on the methods of chemical sample treatment used in the experiment is given in Vol. II, Chapter 6. In the necessary redox steps for valency adjustment, both ferrous solutions and hydroxylamine solutions have been taken for reduction. For oxydation, most laboratories used Na_2NO_2, some $HClO_4$. To separate U and Pu, the ion exchange reaction is preferably employed. Also solvent extraction has been applied. Two laboratories did not separate U and Pu, both were run on the same filament.

A relationship could not be established between the methods and the quality of results. It should be mentioned that with the small analytical quantities involved there is a particularly high risk of cross contamination.

Commercial single stage thermion mass spectrometers were used in general, special made double stage instruments in 4 cases. Clear correlations between the type of instrument and the quality of the results could not be detected with the exception of the expected higher performance of the double stage instruments in the determination of minor isotopes due to the higher abundance sensitivity. No outstanding details on the mass spectrometric measurement techniques applied were reported. A survey on the methods used for mass discrimination correction is given in Vol. II, Chapter 7.

With regard to the determination of the isotope Pu-238, α-spectrometery was preferred by most laboratories. Details on the measurement techniques reported are summarized in Vol. II, Chapter 8.

For preparing the α-source, seven laboratories directly evaporated a solution drop, three laboratories used the electrodeposition method and one laboratory the method of Kirby. As source support stainless steel discs, tantalum discs and platinum ones were used. Pre- amplifiers, linear amplifier and multi-channel pulse weight analyzers were applied, most of them are commercially available types. Surface barrier detectors were used by all the laboratories, the detector resolution is on average about 20 KeV at 5.50 MeV. Generally speaking, the methods and instruments applied seem to be equivalent, deviations observed may be caused by the different methods of treatment of α-spectra data.

Concerning the X-ray fluorescence measurements, reference is made to Vol. II, Chapter 9.

2.5 Reporting of Data and Their General Treatment

The data from all the measurements which had been executed in the laboratories were sent to Karlsruhe on data sheets which had been specially prepared by the evaluation group. In order to guarantee confidential treatment, immediately after their arrival they were marked with the code number assigned to the respective laboratory[1] and separated from any enclosed letter.

The laboratories had been asked to report the isotopic ratios of the single mass spectrometer scans, corrected for instrumental peculiarities as mass discrimination, background etc.. In Fig. 2-9 an example for such a data sheet is given.

In a few cases, the laboratories informed the evaluation group about necessary corrections and supplied the corresponding data. The calculations were then done in Karlsruhe. The experience was made that the specific treatment required for such subgroups of data reported different to the demands increased the delay and the probability of errors in the evaluation of the experiment in an unexpected high manner.

For further treatment, the data were given on punch cards. In order to check for errors which may have happend during this procedure or already before in data transmission to the evaluation group, the numbers of each series of 10 repetition measurement values was examined by application of the Dixon outlier criterion. The details of this procedure are described in Vol. II, Chapter 10. Also references of the original papers of Dixon can be found in this report.

The most frequent errors were the omission of zeros, e.g. 0.037 instead of 0.0037, mix-up of digits, e.g. 0.7593 instead of 0.7953, or wrong orders of magnitude. In quite a few of these cases the laboratories have been contacted in order to allow a meaningful correction of obvious mistakes. Anyhow, this check was designed with the aim to detect strongly deviating measurement results with a low probability of error, keeping in mind that it should be avoided to simulate a false precision of the measurements by omission of too many "outliers". After this outlier

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[1] Numbers up to 23 - but not all - were used as codes.

Standard Experiment

Sample: A (unspiked) - Plutonium Code: 16

(For α-spectrometric data, see II-39)

Date of chemical preparation: ... October 31, 1972

Filament No: 2 Date of MS-Measurement: ... October 31, 1972

Scan No.:	Atomic Ratio			
	238/239	240/239	241/239	242/239
1	01620 0.----	2326 0.----	1264 0.----	02298 0.----
2	0.01622	0.2317	0.1263	0.02300
3	0.01619	0.2319	0.1263	0.02298
4	0.01630	0.2320	0.1262	0.02312
5	0.01639	0.2329	0.1267	0.02311
6	0.01642	0.2333	0.1269	0.02306
7	0.01635	0.2334	0.1268	0.02297
8	0.01636	0.2330	0.1265	0.02306
9	0.01648	0.2321	0.1268	0.02306
10	0.01648	0.2340	0.1266	0.02305

Don't use this space!

Remark:

Fig. 2-9: IDA-72: Sheet for Data Reporting (Example) selection the first 8 of the remaining values were used for the subsequent calculations.

This outlier check is the first part of an extensive program system developed for the standard experiment to calculate the mean values and variances, to determine the isotopic composition of the given solutions including the results of α-spectrometry and finally the uranium and plutonium concentrations for the main isotopes as well as for the elements as such.

Also some of the additional experiments were evaluated by this computer program.

The ≈ 30 000 numerical values as well as the program system are stored on a disc. An IBM 370/185 computer needs about 1 minute and 480 000 bytes of storage to perform all the computations mentioned. The program is described and listed in Vol. II, Chapter 11. The complete computer output for one laboratory is given as an example in Vol. II, Chapter 12.

To illustrate how the calculation of mean values and estimates for variances in the statistical evaluation of the isotopic ratio determinations was made, Fig. 2-10 gives a schematic view of the analysis.

The values X_{ijk} of this figure are the reported single scan results of a certain isotopic ratio of uranium or plutonium[1].

The indices stand for

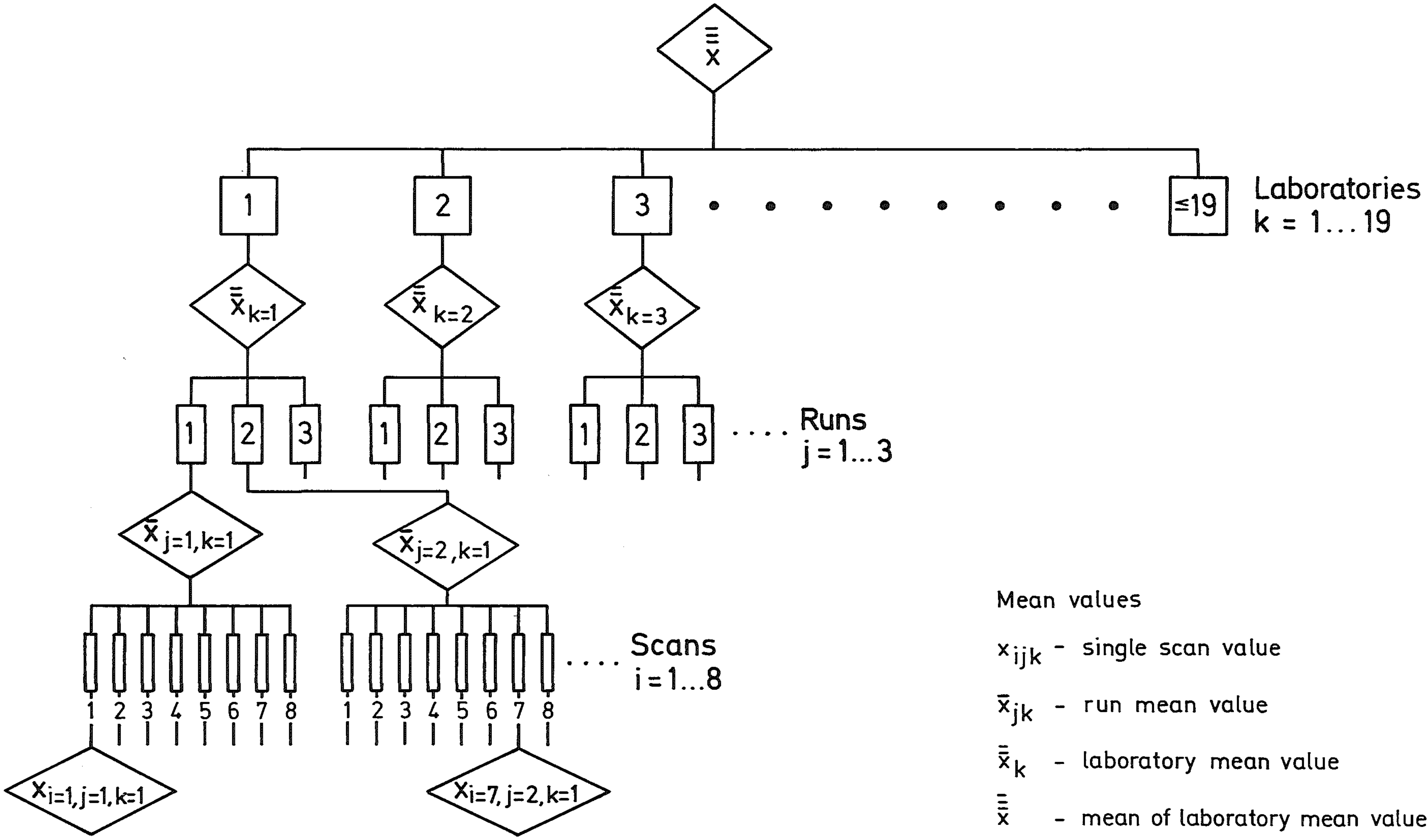
i - number of the scan
j - number of the run
k - number of the laboratory.

In a first part of the computer program the run mean value was calculated for the 8 scan values:

$$\bar{X}_{jk} = \frac{1}{8} \sum_{i=1}^{8} X_{ijk}$$

---

[1] These reatios were always determined in relation to the most abundant isotope, i.e. U-233 and Pu-242, respectively, for the spike solutions, U-238 and Pu-239 for all the other sample solutions.



Mean values

x_{ijk} - single scan value

$\bar{x}_{jk}$ - run mean value

$\bar{\bar{x}}_{k}$ - laboratory mean value

$\bar{\bar{x}}$ - mean of laboratory mean values

Fig. 2-10 IDA-72: Layout for the Data Evaluation

In a next part the laboratory mean value is calculated according to the expression

$$\bar{\bar{X}}_k = \frac{1}{3} \sum_{j=1}^{3} \bar{X}_{jk}$$

as three runs per sample were performed in general.

From these laboratory mean values the "mean of means" for each ratio and sample can be obtained as

$$\bar{\bar{\bar{X}}} = \frac{1}{19} \sum_{k=1}^{19} \bar{\bar{X}}_k$$

under the assumption that 19 laboratories have measured the ratio. In case some of the laboratories were unable to determine a certain isotopic ratio – e.g. because of insufficient measurement sensitivity – the formulae were adjusted accordingly.

In most of the following figures of this report the laboratory mean values $\bar{\bar{X}}_k$ are compared with the "mean of means" by giving the "mean of means" as zero line and depicting the relative deviations of the laboratory mean values from this over-all-mean, expressed as percentage:

$$\frac{100}{\bar{\bar{\bar{X}}}} \cdot (\bar{\bar{X}}_k - \bar{\bar{\bar{X}}})$$

The error bars assigned to the laboratory mean values $\bar{\bar{X}}_k$ in these figures indicating the 1 σ-ranges are defined by

$$\frac{100}{\bar{\bar{X}}_k} \sigma_k = \frac{100}{\bar{\bar{X}}_k} \left(\frac{\sum_{j=1}^{3} (\bar{X}_{jk} - \bar{\bar{X}}_k)^2}{3 \cdot 2} \right)^{\frac{1}{2}}$$

Concerning the well known formulae for calculating isotopic compositions reference is made to Vol. II, Par. 11.2.10, for the concentration calculations to Par. 3.5.1 of this volume.

For all the mean values defined before (run mean, laboratory mean and mean of the laboratory means)[1] estimates of their variances can be

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[1] In a strict sense, the definition of the mean values on which the analyses of variances are based is somewhat different. However, for the orthogonal case, the numerical values are identical.

calculated by analysis of variances as indicated in the layout for the data evaluation given in Fig. 2-10.

These estimate values of the variances correspond to three error components named scan, run and interlaboratory error component,all contributing to the total error of any isotopic ratio determination.

Different to the case of the isotopic ratio determinations, the total error of the concentration determinations is split into two components only, named precision and interlaboratory deviation. The reason is that any single concentration determination of a laboratory is always based on the run mean values of the isotopic ratio measurements and not on single scan values. As according to the experimental layout /Par.3.1/ each run mean value of the ratio spike isotope/ most abundant isotope in the spiked solution (this ratio is the determing term for the concentration value) belongs to a separate chemical sample preparation procedure, the variance of repetition analyses within the laboratories describes the error component precision. It should be noted that - as usual - a high precision is indicated by low numerical values. The interlaboratory deviation is given by the variance of the laboratory mean values as in the case of the isotopic ratios discussed before.

Instead of the numerical values of variances in this report in general those of the corresponding relative standard deviations are given because the latter are preferred in practical use.

The formulae for the calculation of the estimates of the error components by analyses of variances are given in Ref. /4/.

The numerical values of all constants used in the calculations are summarized in Vol. II, Chapter 1.

Due to their high number, it was not possible to include all the initial data reported by the laboratories in this paper. However, a list of the laboratory mean values and the scan and run variances per laboratory for all isotopic ratios of all solutions measured in the standard experiment is given in Vol. II, Par. 12.3.

3. Evaluation of the Standard Experiment

3.1 Layout and Participation

A scheme of the analytical procedures followed by the laboratories in the standard experiment is given in Fig. 3-1.

For the spiked sample material the performance of three independent chemical sample preparations was requested in order to study the influence of these procedures on the reproducibility of the measurements. A survey on the methods of chemical sample preparation used by the laboratories is given in Volume II, Chapt.6.

It should be noted that error contributions caused by these steps (valency adjustment, U/Pu-separation) may strongly influence the isotopic ratios U-233/U-238 and Pu-242/Pu-239 of the spiked samples, but would be of minor effect only on all the other isotopic ratios because of the nearly monoisotopic composition of the spike material (about 98% for U-233 and Pu-242, respectively, in the mixed spike solution /Tab. 2-1/). Only cross contamination which may happen during sample preparation could influence any isotopic ratio.

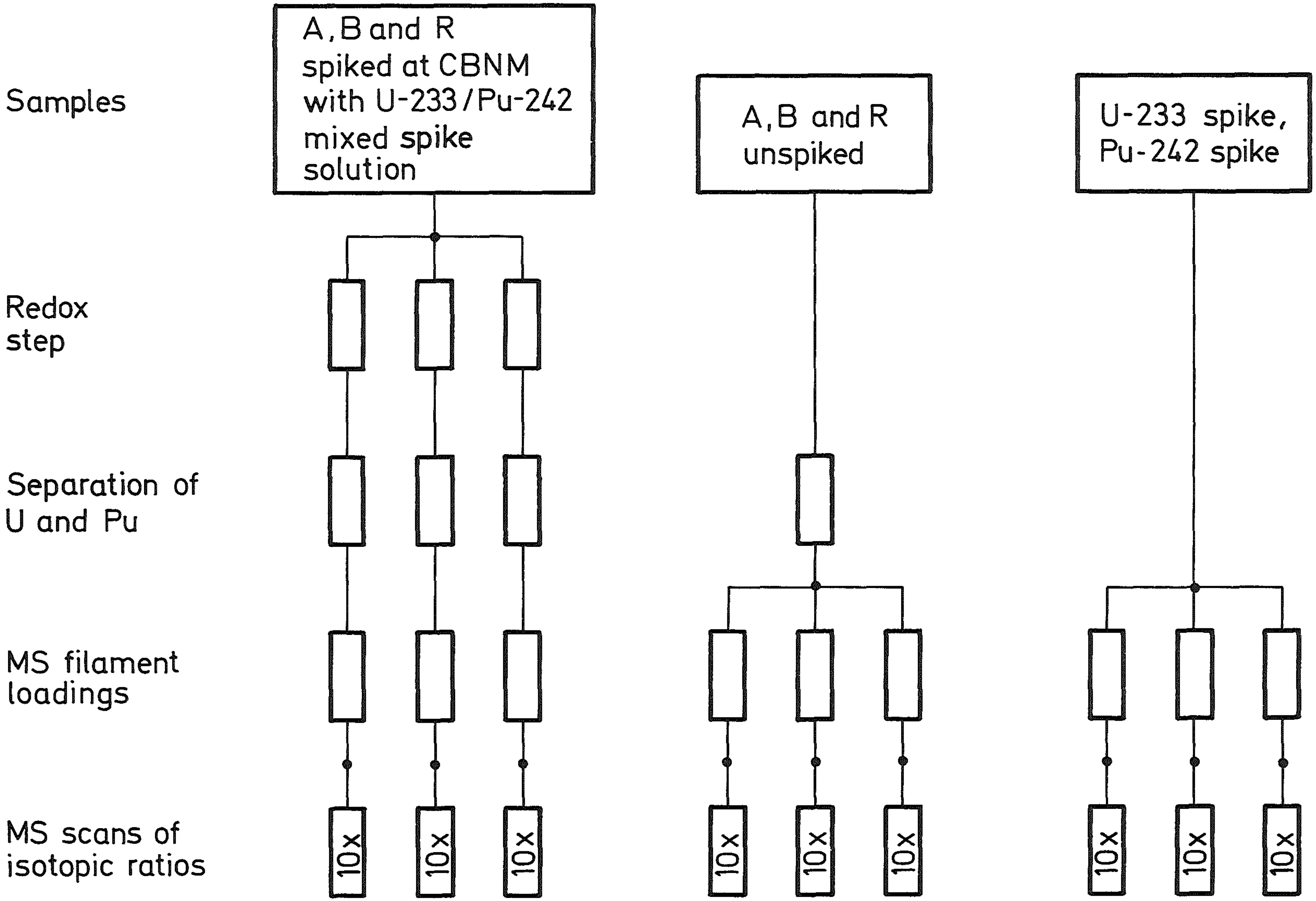
For the unspiked samples, repetition of the U/Pu separation steps did not seem meaningful because of their chemically uniform composition.

The single U-233 and Pu-242 components of the mixed spike solution were shipped to the laboratories separately and therefore no separation became necessary for these materials /Par. 2-1/.

In total 19 laboratories participated in this test and performed the analyses in accordance with the demands,but with the following exceptions:

Lab. 23	reported no plutonium measurements.
Lab. 16	supplied data of unspiked samples only. Therefore, no concentration values could be calculated.
Lab. 2 and Lab. 23	loaded samples directly onto filaments without chemical pretreatment.
Lab. 15 and Lab. 20	performed more than one chemical separation for the unspiked samples.

Fig. 3-1 IDA-72: Analytical Procedures of the Standard Experiment



(•) indicate branching points

Concerning the basic reported data and their general treatment reference is made to Par.2.5.The calculated laboratory mean values of all isotopic ratios and their standard deviations are compiled in Vol. II, Par.12.3.

In the graphical presentations given in the following paragraphs, principally the code numbers are indicated for all laboratories which participated in this part of the experiment. These code numbers are put in round brackets, if for any reason the laboratory could not supply data for the measurement in question.

Laboratory mean values which were considered as outliers and were therefore not used for the calculation of the mean of the laboratory means are put in square brackets. For this rejection of laboratory mean values as outliers no strict rule was followed. If there was no clear evidence, in some cases use was made of the basic principals of the Dixon criterion as a help for decision,although this criterion is delineated for the rejection of individual observations rather than of the mean values of data.

3.2 Isotopic Ratio Determinations by Mass Spectrometry

3.2.1 Uranium Measurements

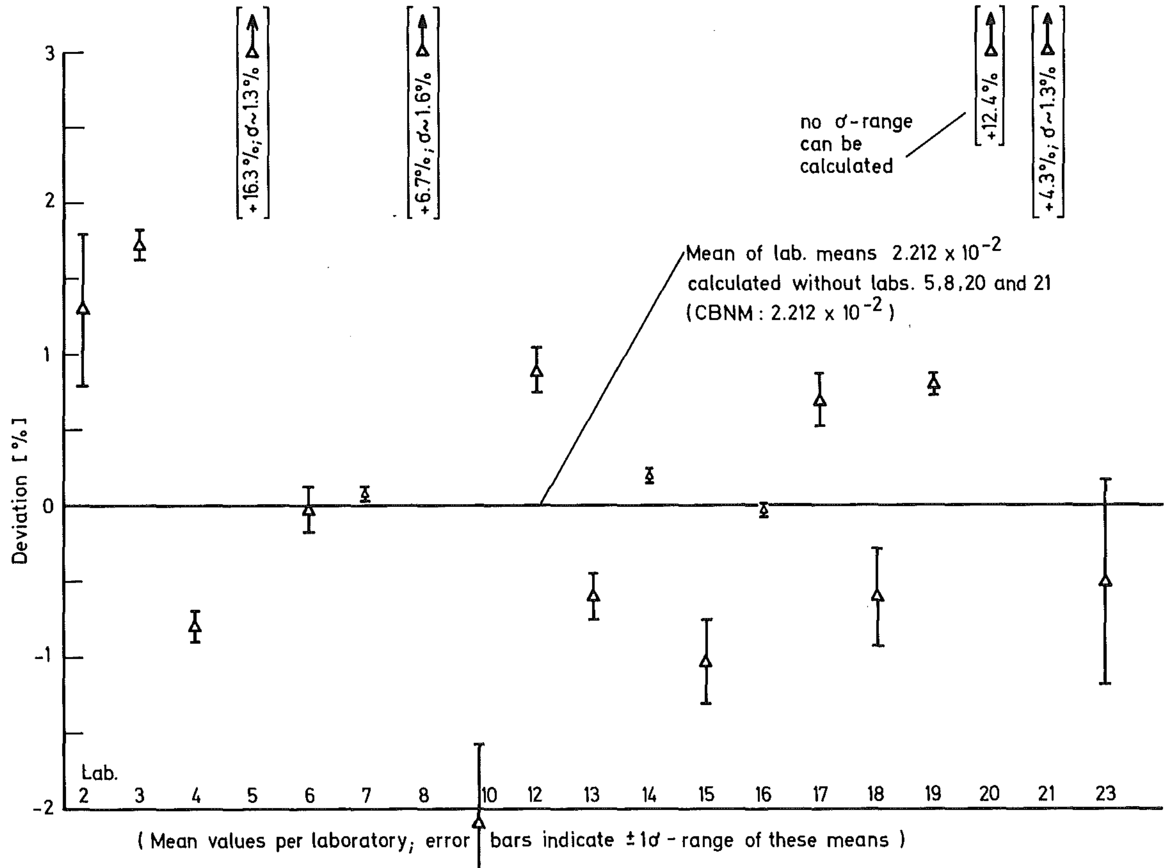
The results of the isotopic ratio determinations on uranium are given

- in Fig. 3-2 for the U-238/U-233 measurements on the single U-233 spike solution;

- in Fig. 3-3 for the U-233/U-238 measurements on the spiked sample solutions A, B and R;

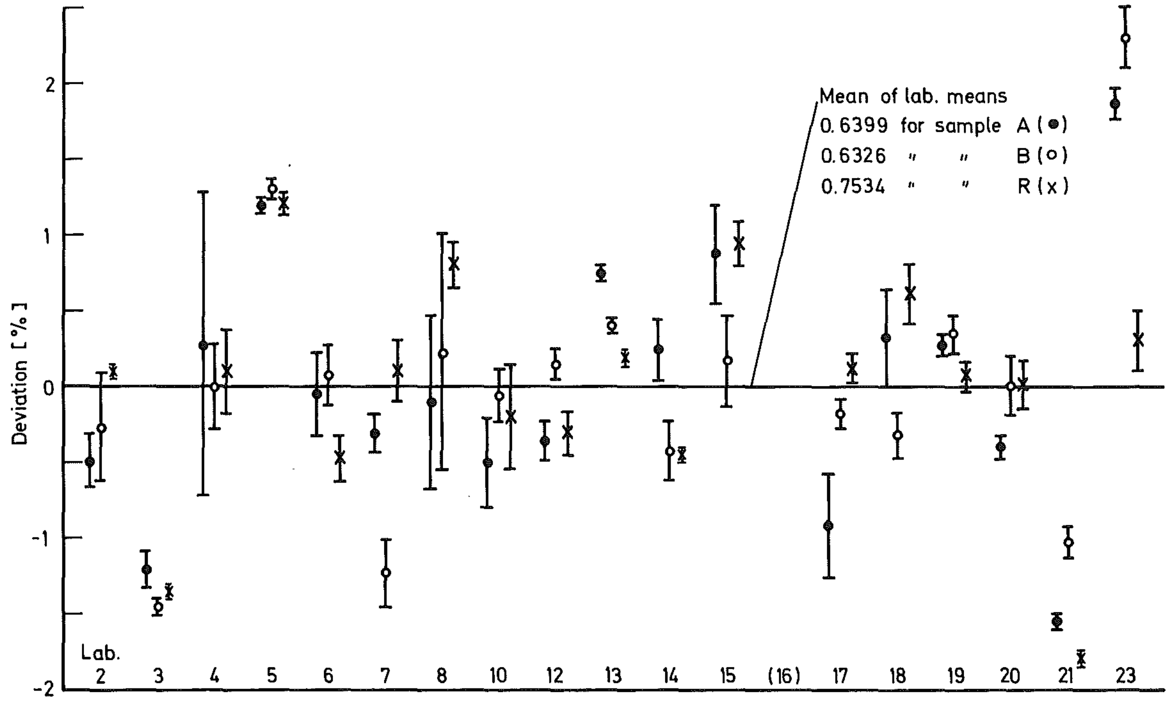
- in Fig. 3-4 to Fig. 3-9 for the U-234/U-238, U-235/U-238 and U-236/U-238 measurements on the unspiked and spiked sample solutions A and B;

- in Fig. 3-10 to Fig. 3-13 for the U-234/U-238 and U-235/U-238 measurements on the unspiked and spiked reference solution R.



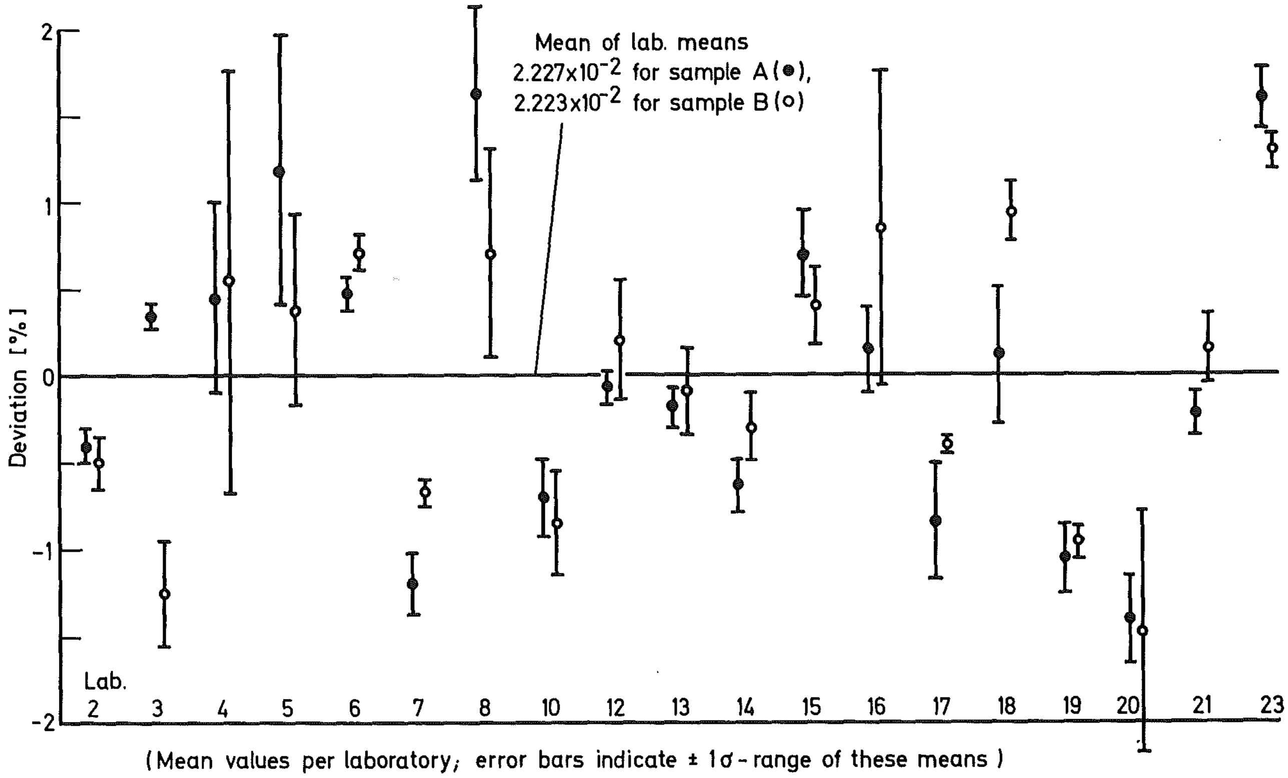
(Mean values per laboratory; error bars indicate ± 1σ - range of these means)

Fig. 3-2 IDA-72 : MS-Determinations of Isotopic Ratio U238 / U233 of U233 Single Spike Solution



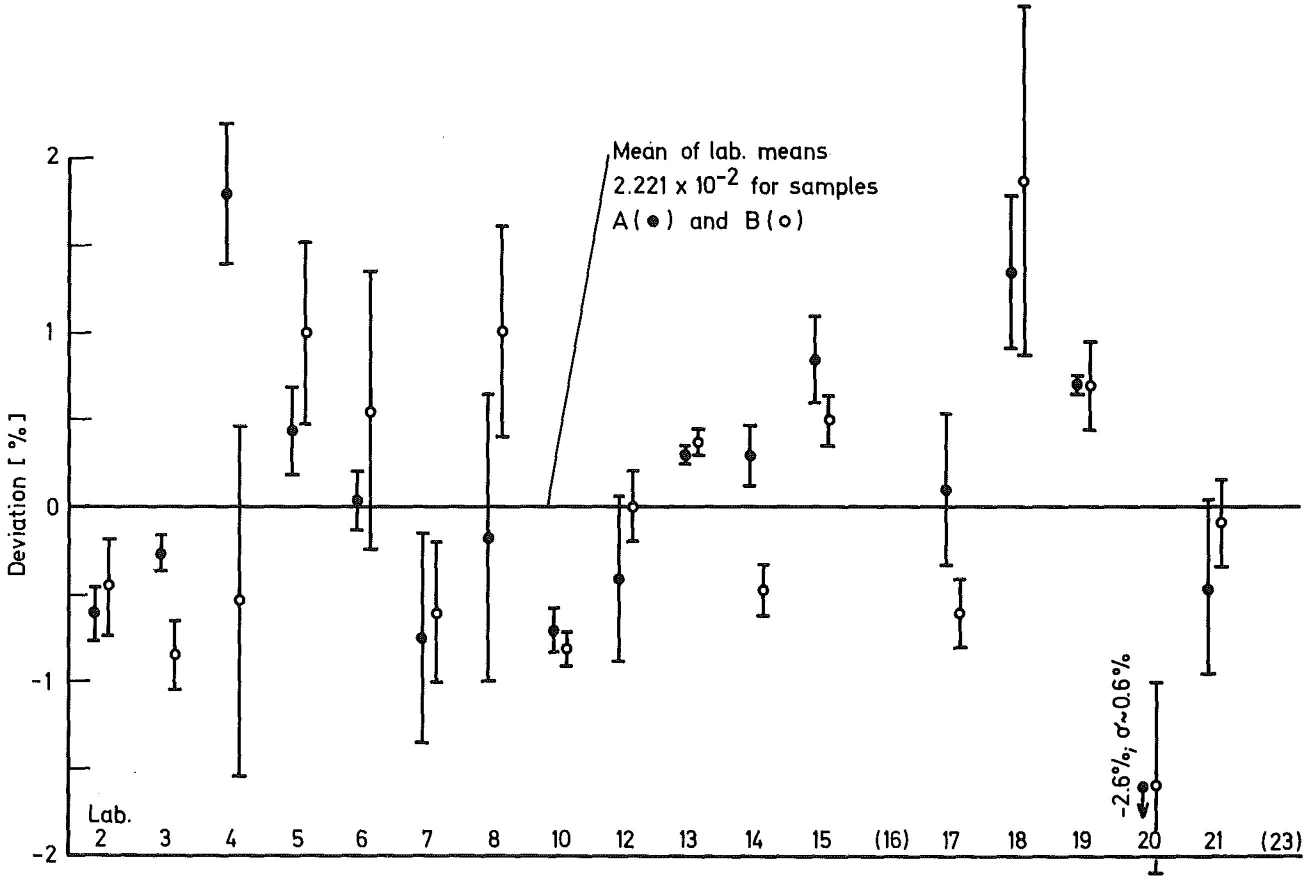
(Mean values per laboratory; error bars indicate ± 1σ - range of these means)

Fig. 3-3 IDA-72 : MS-Determinations of Isotopic Ratio U233 / U238 of Spiked Samples A, B and R



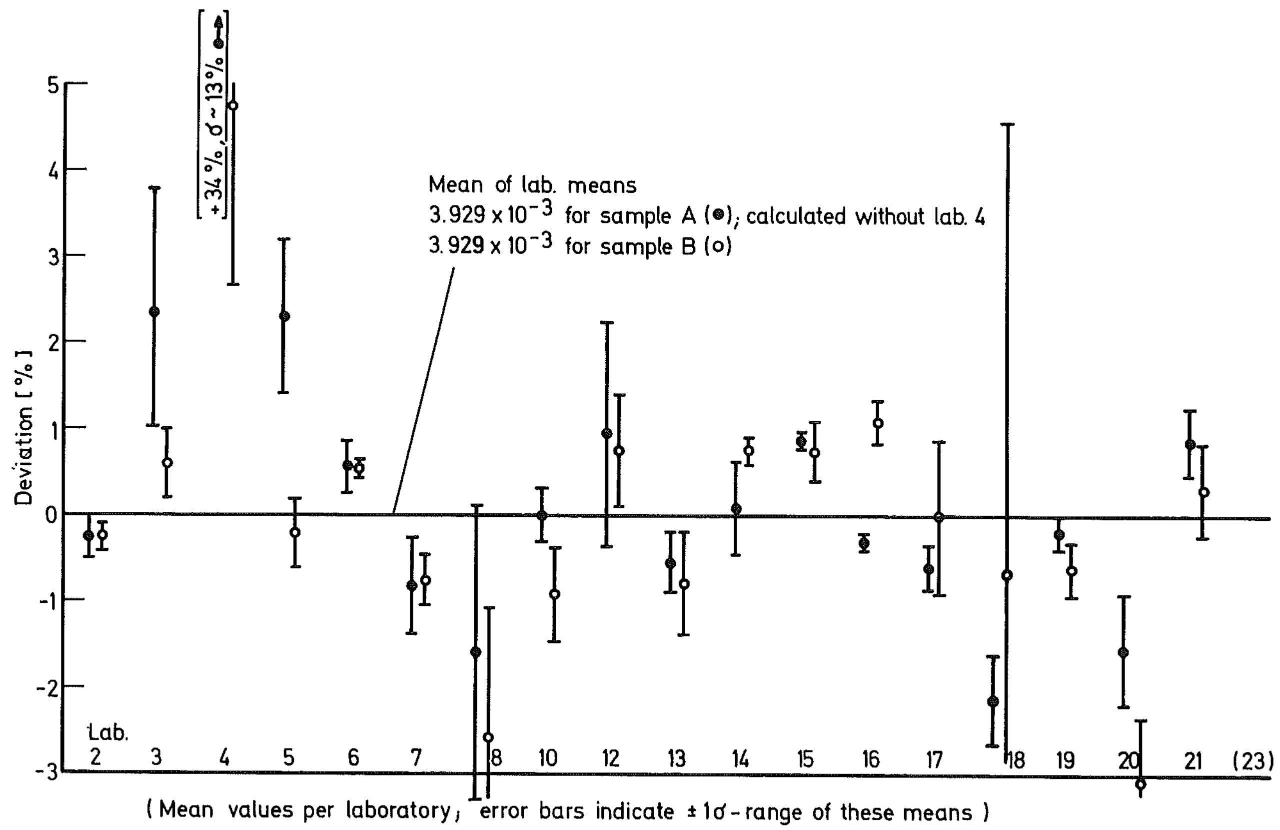
(Mean values per laboratory; error bars indicate ± 1σ-range of these means)

Fig. 3-4 IDA-72: MS-Determinations of Isotopic Ratio U235/U238 of Unspiked Samples A and B



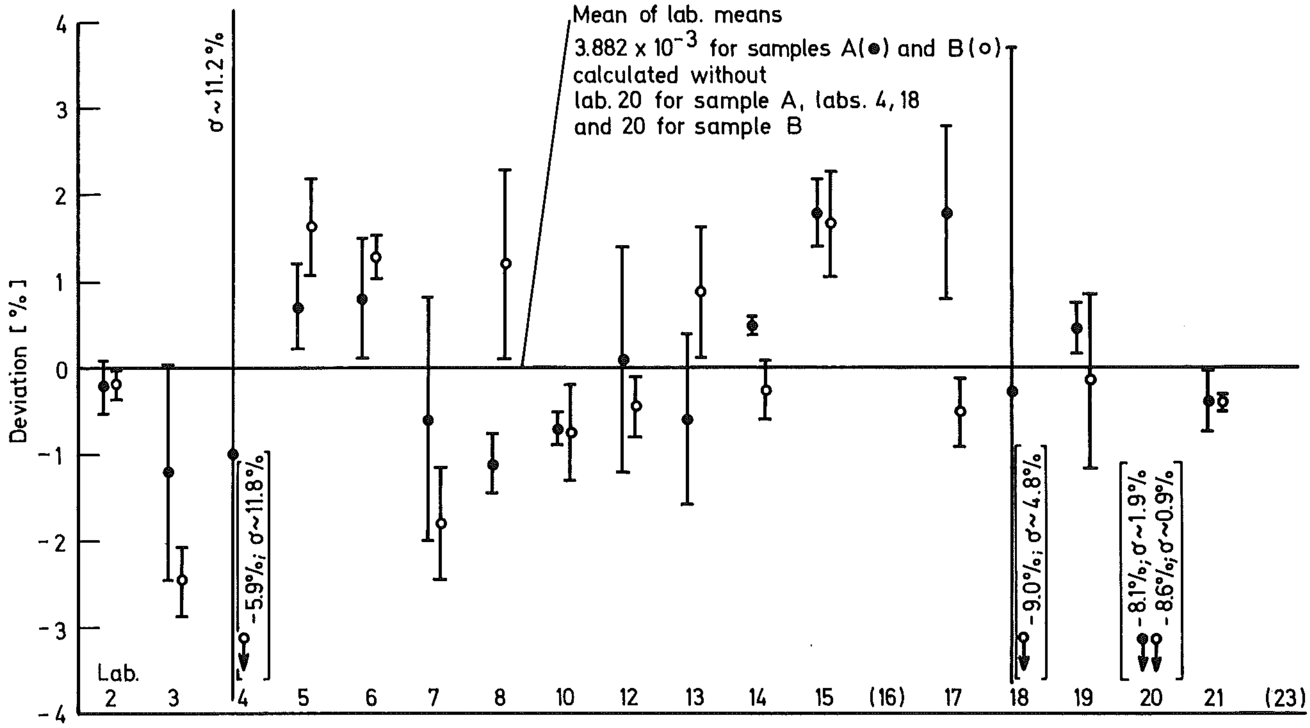
(Mean values per laboratory; error bars indicate ± 1σ-range of these means)

Fig. 3-5 IDA-72: MS-Determinations of Isotopic Ratio U235 / U238 of Spiked Samples A and B



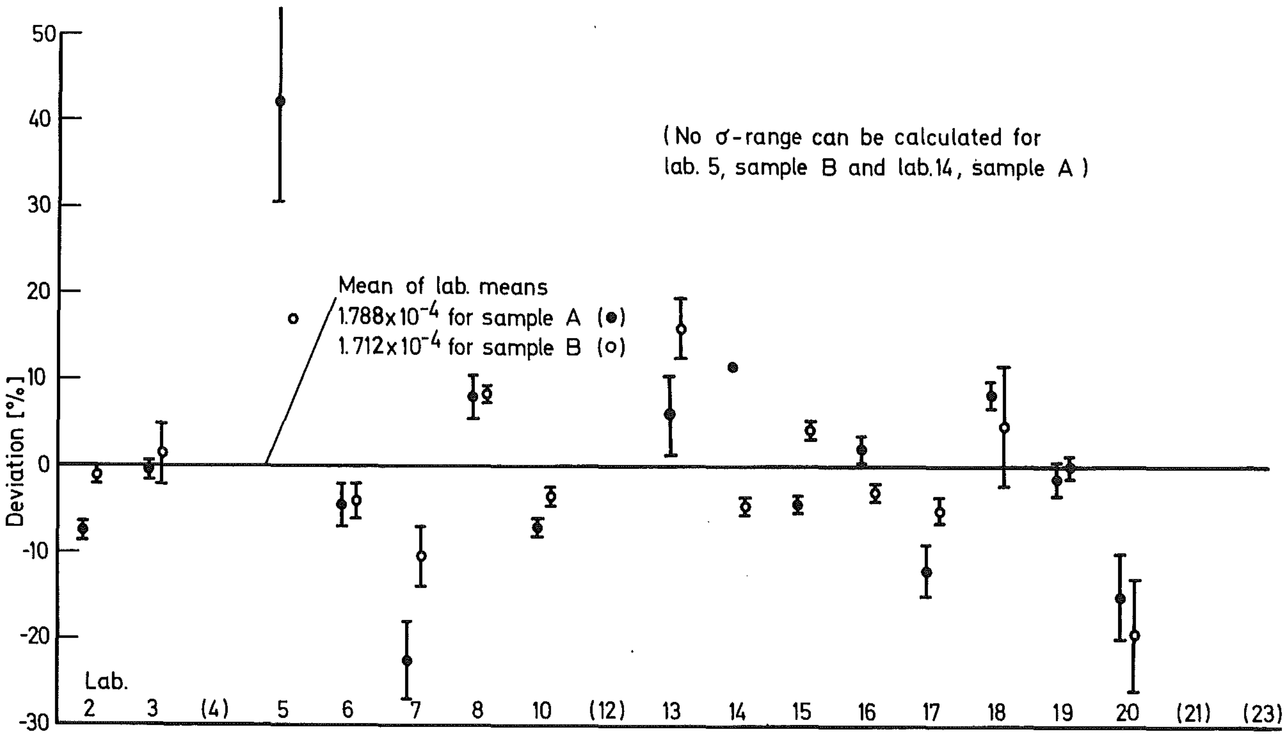
(Mean values per laboratory; error bars indicate ± 1σ - range of these means)

Fig.3-6 IDA-72: MS-Determinations of Isotopic Ratio U236/U238 of Unspiked Samples A and B



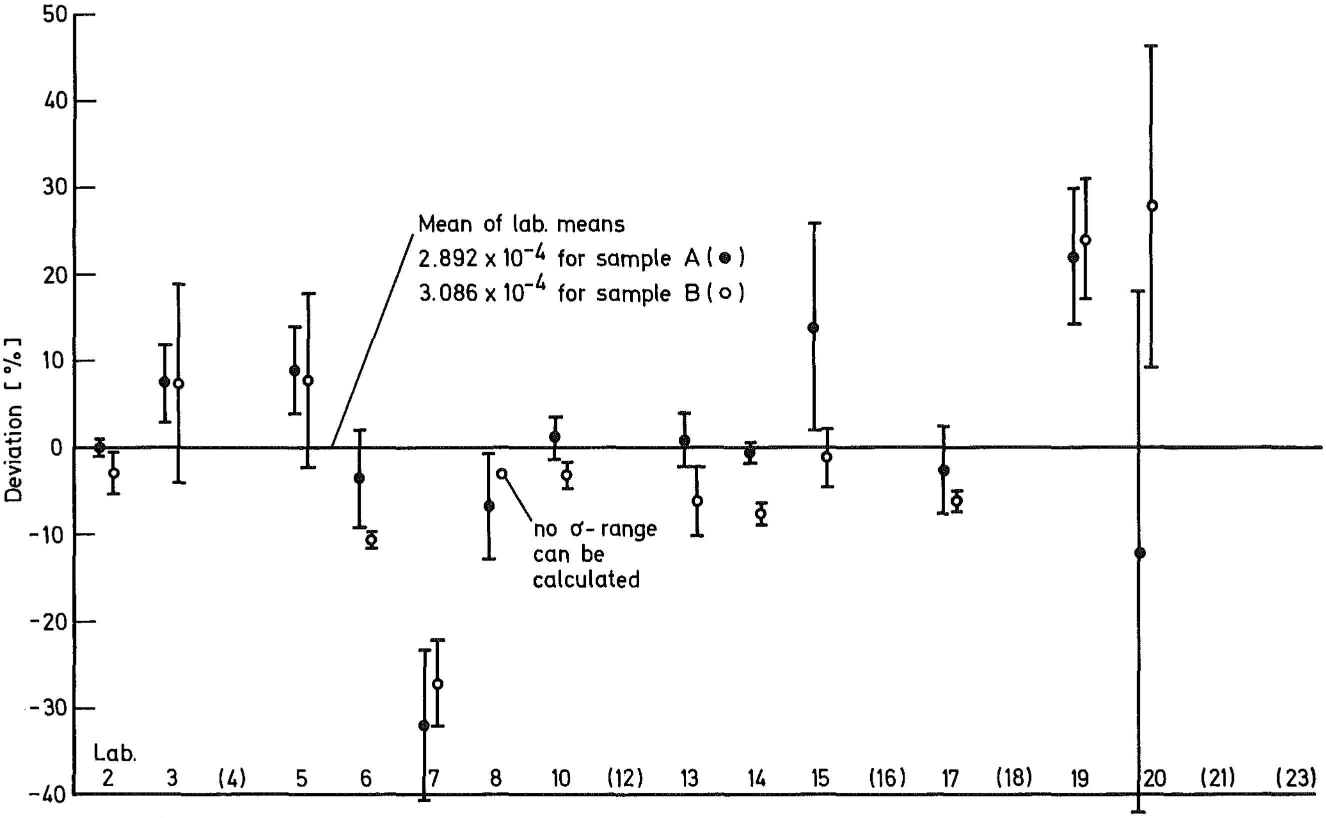
(Mean values per laboratory; error bars indicate ± 1σ - range of these means)

Fig. 3-7 IDA-72: MS-Determinations of Isotopic Ratio U236 / U238 of Spiked Samples A and B



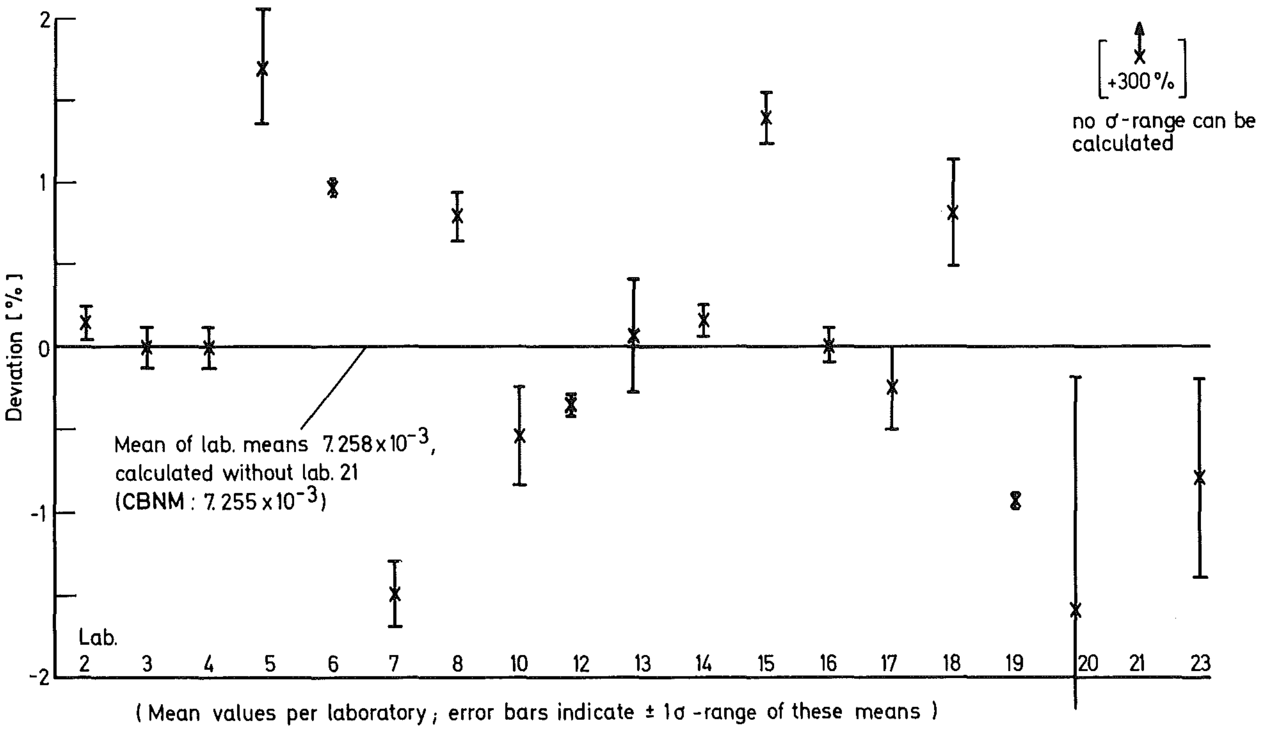
(Mean values per laboratory; error bars indicate ± 1σ - range of these means)

Fig. 3-8 IDA-72: MS-Determinations of Isotopic Ratio U234/U238 of Unspiked Samples A and B



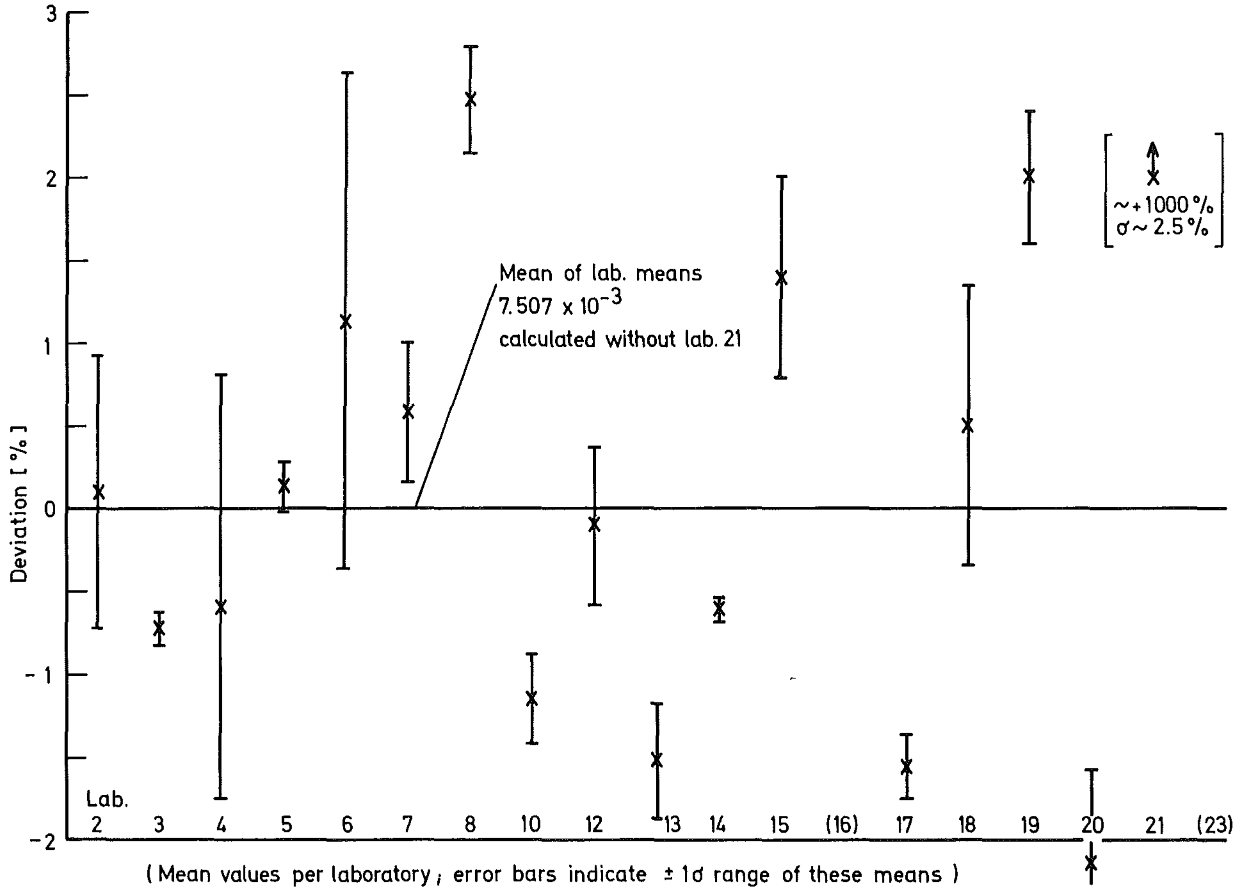
(Mean values per laboratory; error bars indicate ± 1σ-range of these means)

Fig. 3-9 IDA-72: MS-Determinations of Isotopic Ratio U234 / U238 of Spiked Samples A and B



(Mean values per laboratory ; error bars indicate ± 1σ -range of these means)

Fig. 3-10 IDA-72 : MS-Determinations of Isotopic Ratio U235 / U238 of Unspiked Sample R



(Mean values per laboratory ; error bars indicate ± 1σ range of these means)

Fig. 3-11 IDA-72 : MS-Determinations of Isotopic Ratio U235 / U238 of Spiked Sample R

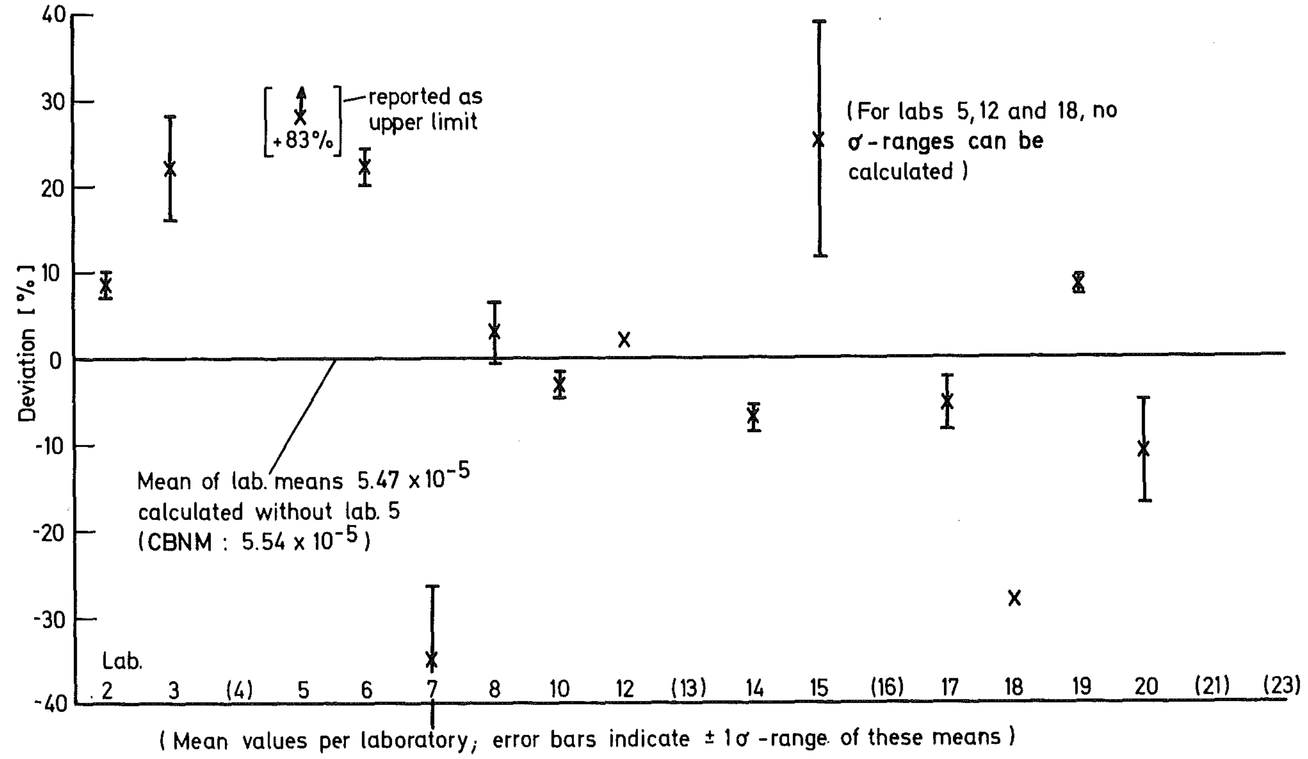


Fig.3-12 IDA-72: Determinations of Isotopic Ratio U234/U238 of Unspiked Sample R

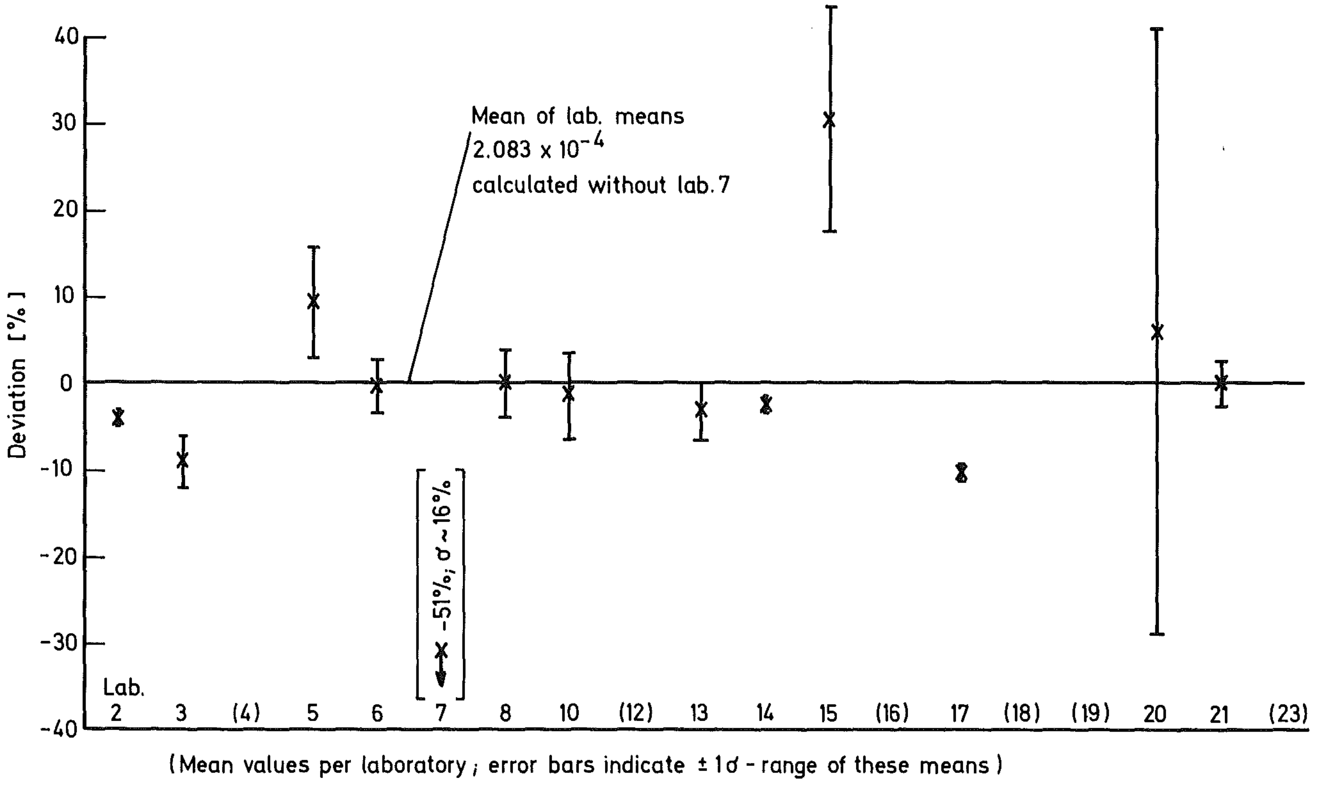


Fig. 3 - 13 IDA-72: MS - Determinations of Isotopic Ratio U234 / U238 of Spiked Sample R

From the results shown in these figures, the following observations and statements can be made:

- In total, 12 of 334 laboratory mean values (3.6%) had to be considered as outliers. Most likely they may be explained by cross contamination with uranium of other isotopic composition.

- In general, the means of the laboratory means calculated for samples A and B are in excellent agreement which is a certain proof that no contamination occured during the preparation of the A and B sample solutions.

- From the measurements on the U-233 single spike solution and the unspiked R sample it can be seen that there is also excellent agreement between the calculated mean of the laboratory means and the values certified by the CBNM.

- In many cases, the deviations of the values obtained for the A and B sample by the same laboratory on a certain isotopic ratio are clearly correlated, indicating a laboratory bias.

- The results indicate the better performance of tandem mass spectrometers compared to single focussing instruments at least for the determination of rare isotopes. However, more detailed information on this subject must not be given in order to avoid a revealing of the codes.

The ratios U-233/U-238 of the unspiked A, B and R samples and U-236/U-238 of the R sample were not taken into consideration because data were reported by very few laboratories only.

3.2.2 Plutonium Measurements

The results of the isotopic ratio determinations for plutonium are given

- in Fig. 3-14 and Fig. 3-15 for the Pu-239/Pu-242 and Pu-240/Pu-242 measurements on the single Pu-242 spike solution;

- in Fig. 3-16 to Fig. 3-21 for the Pu-238/Pu-239, Pu-240/Pu-239 and Pu-241/Pu-239 measurements on the unspiked and spiked samples A and B as well as for the Pu-242/Pu-239 measurements on the unspiked A and B sample solutions;

- in Fig. 3-22 to Fig. 3-26 for the Pu-240/Pu-239 and Pu-241/Pu-239 measurements on the unspiked and spiked reference solution R as well as for the Pu-242/Pu-239 measurements on the unspiked R-sample;

- in Fig. 3-27 for the Pu-242/Pu-239 measurements on the spiked sample solutions A, B and R.

In order to obtain comparable data, the values reported for the isotopic ratio Pu-241/Pu-239 were corrected for the α-decay of the Pu-241 isotope, as the sample age was different at the time of analysis in the individual laboratories.1) 15.10 years was used as half life period /Vol. II, Chapt. 1/. June 21st, 1972, the date of sampling at EUROCHEMIC, was chosen as reference date for the A and B samples, January 20th, 1972 for the R-sample, as the certificate of the CBNM for the isotopic composition of this material refers to this date.
Lab. 2 made no separation of americium. Therefore, its measurements of Pu-241/Pu-239 were not used for the calculation of the mean values in the corresponding figures. Only a few laboratories reported data on the Pu-238/Pu-239 ratio because the majority of the laboratories performed these determinations by α-spectrometry /Par. 3.3/.

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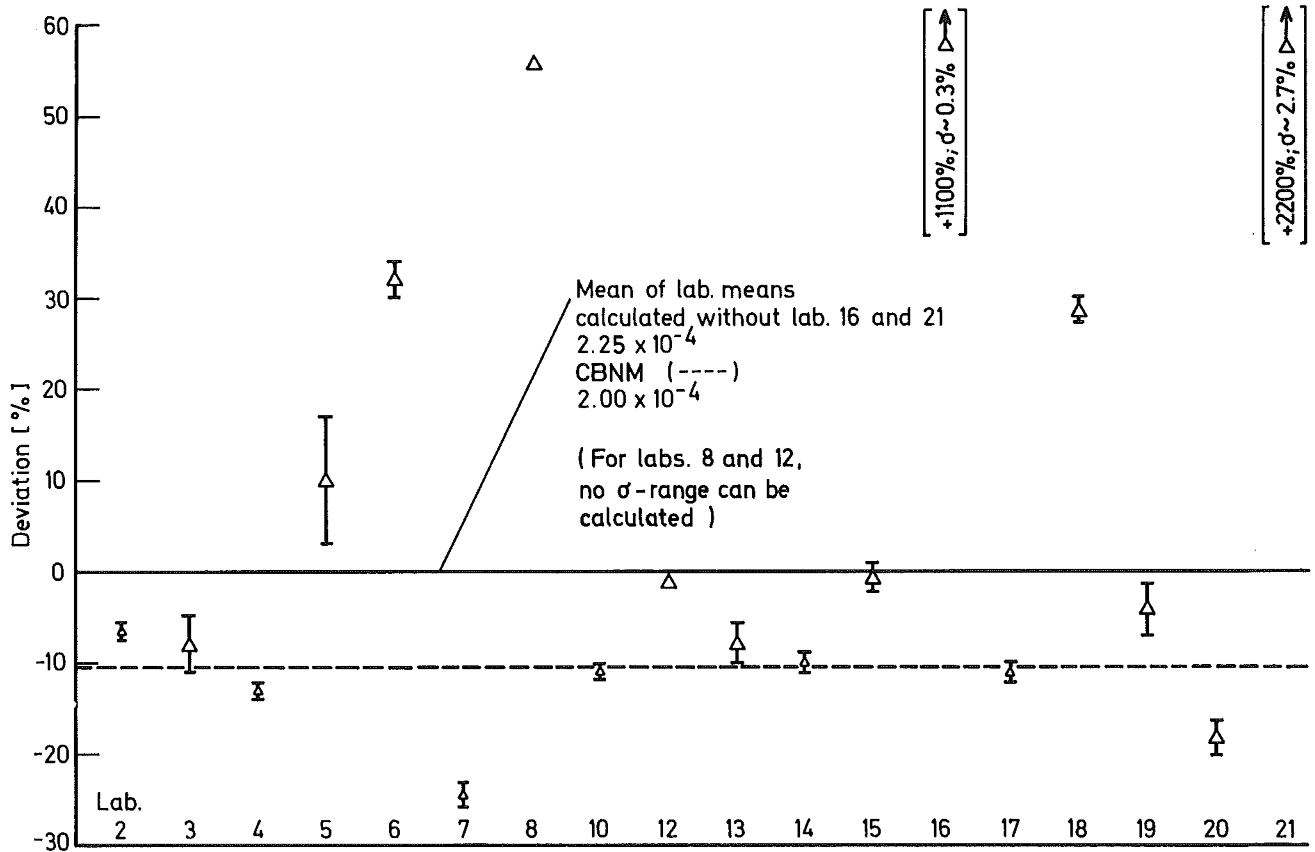
1) The time intervals for the corrections of the individual laboratories are given in Vol. II, Par. 11.4, program MAIN, statements 0041 to 0233. This part of the computer program is explained in Vol. II, Par. 11.2.2.



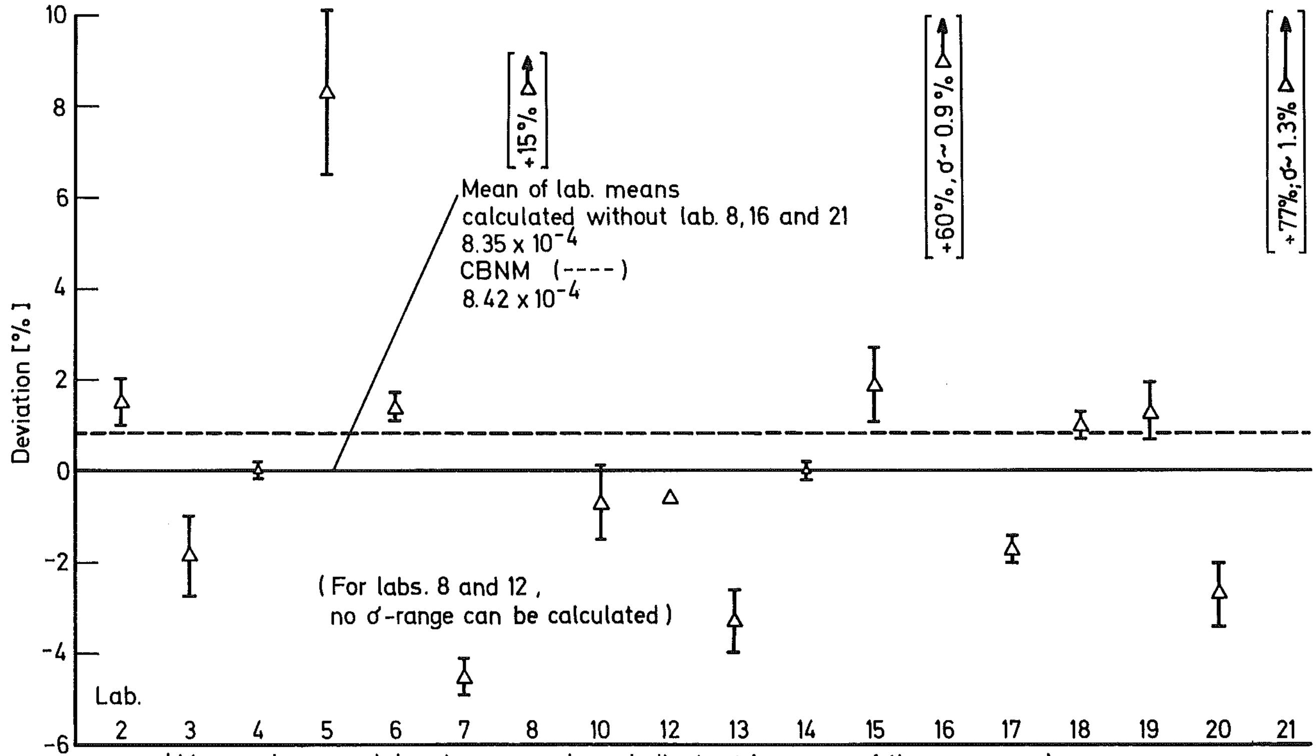
Mean of lab. means calculated without lab. 16 and 21 2.25×10^{-4}

CBNM (----) 2.00×10^{-4}

(For labs. 8 and 12, no σ-range can be calculated)

(Mean values per laboratory; error bars indicate ± 1σ-range of these means)

Fig.3-14 IDA-72: MS-Determinations of Isotopic Ratio Pu 239/Pu 242 of Single Pu 242 Spike Solution



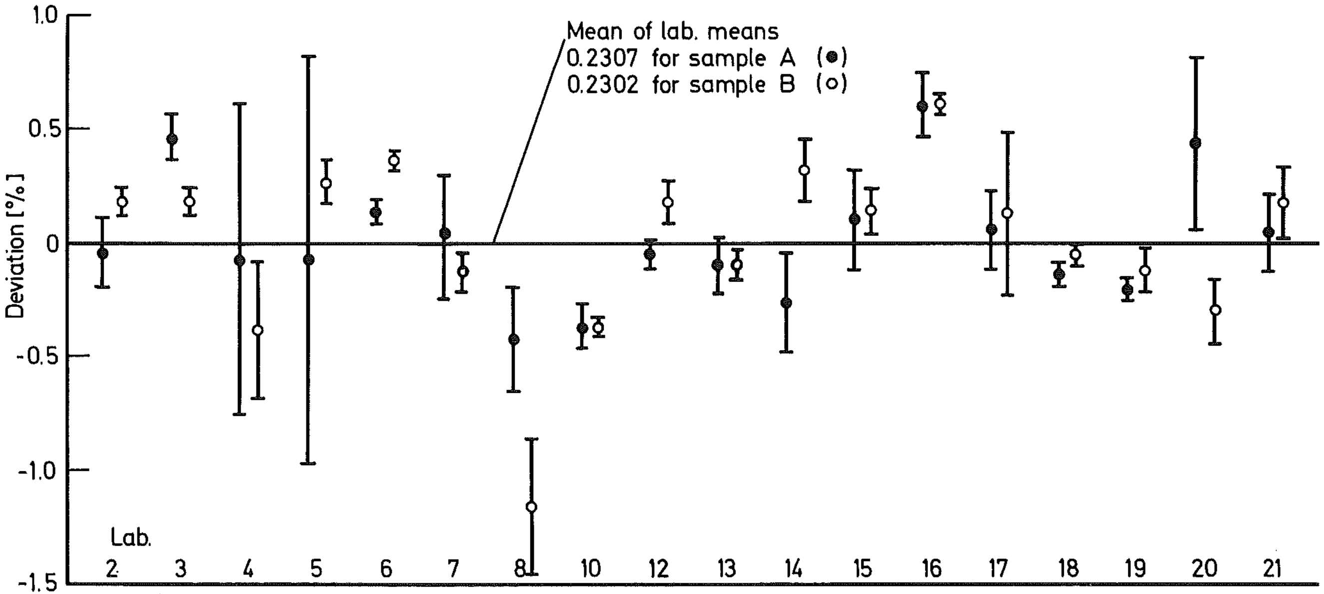
Mean of lab. means calculated without lab. 8, 16 and 21 8.35×10^{-4}

CBNM (----) 8.42×10^{-4}

(For labs. 8 and 12, no σ-range can be calculated)

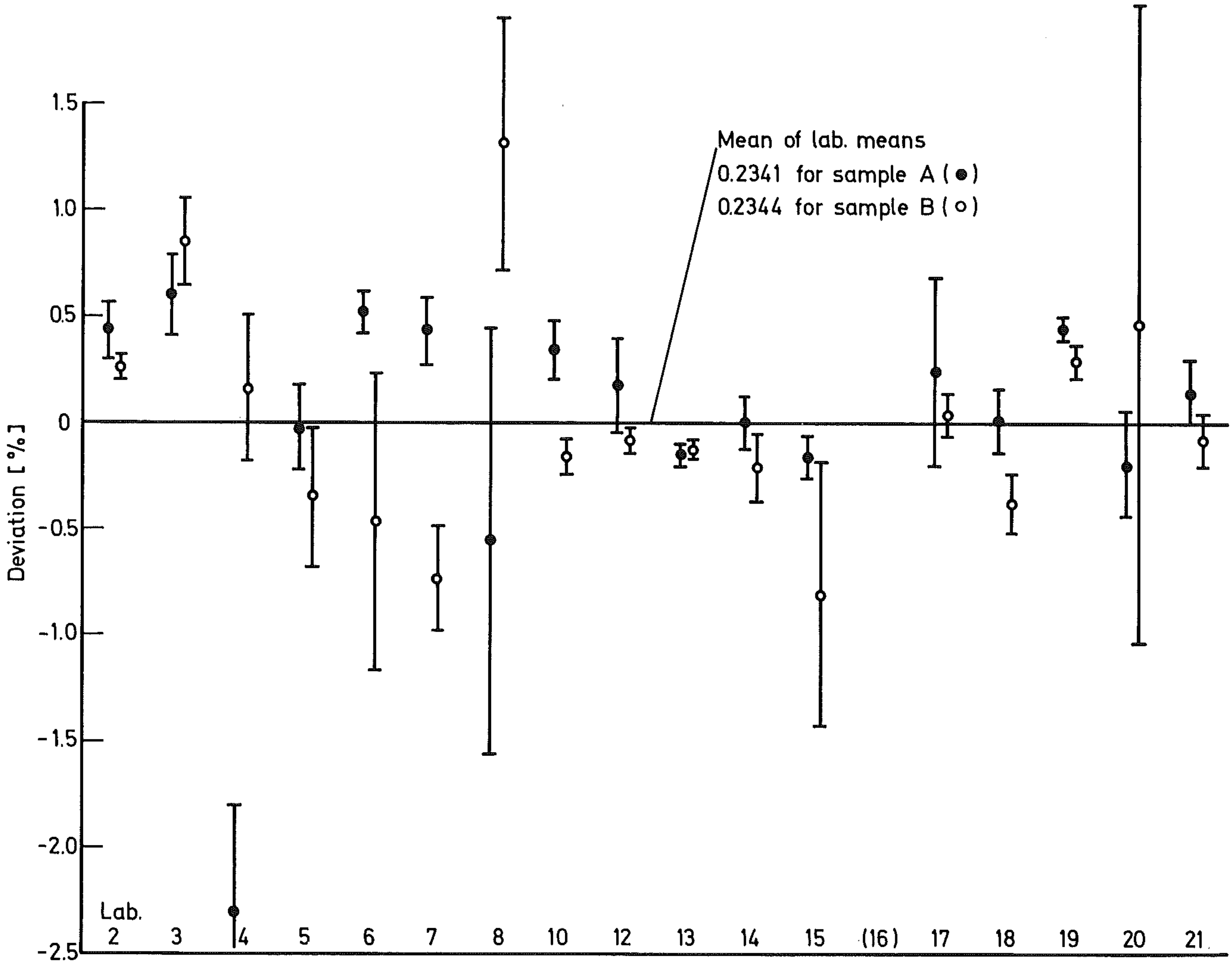
(Mean values per laboratory; error bars indicate ± 1σ-range of these means)

Fig.3-15 IDA-72: MS-Determinations of Isotopic Ratio Pu 240/Pu 242 of Single Pu 242 Spike Solution



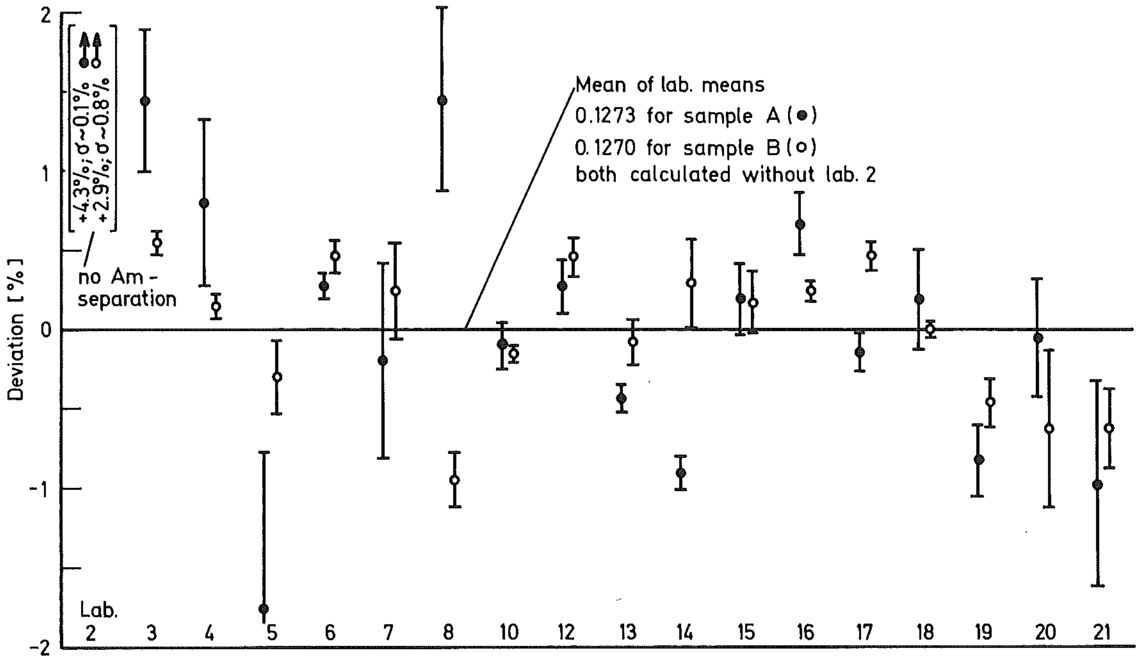
(Mean values per laboratory; error bars indicate ± 1σ-range of these means)

Fig. 3-16 IDA-72: MS-Determinations of Isotopic Ratio Pu240/Pu239 of Unspiked Samples A and B



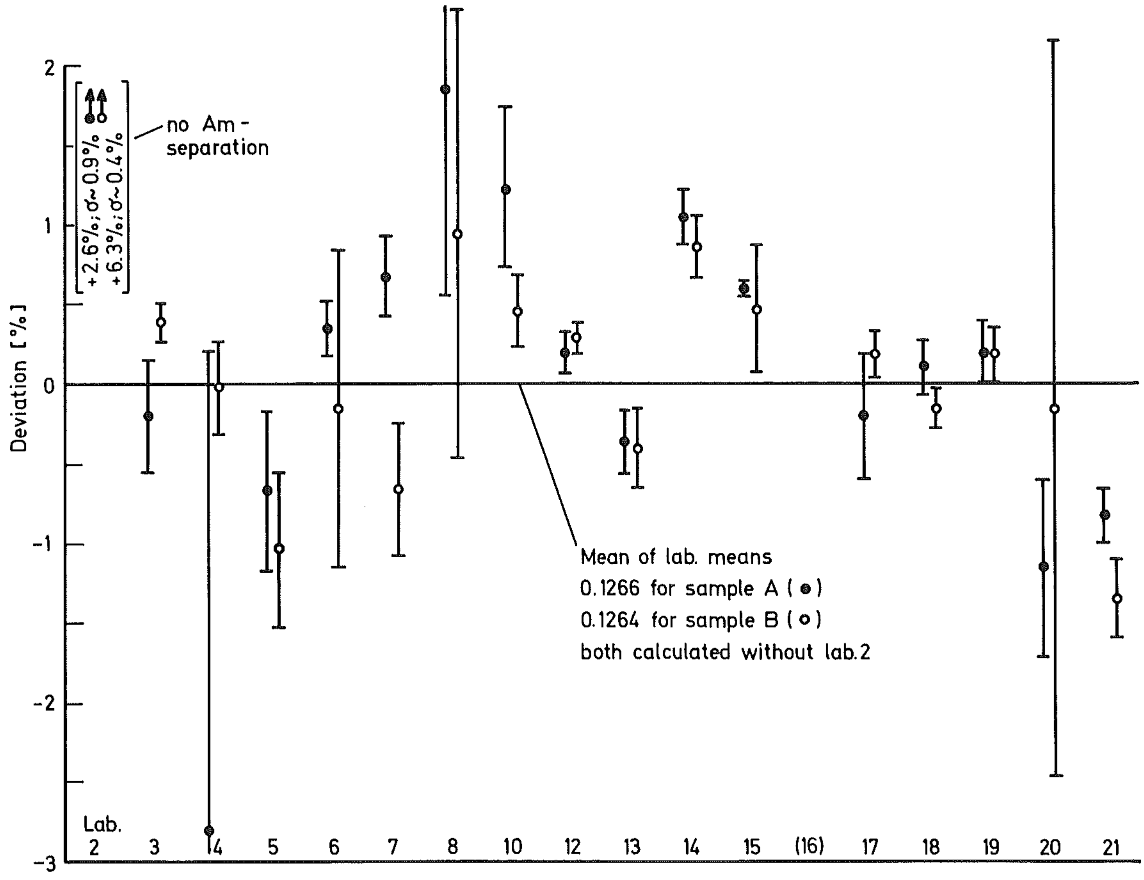
(Mean values per laboratory; error bars indicate ± 1σ-range of these means)

Fig. 3-17 IDA-72: MS-Determinations of Isotopic Ratio Pu 240 / Pu 239 of Spiked Samples A and B



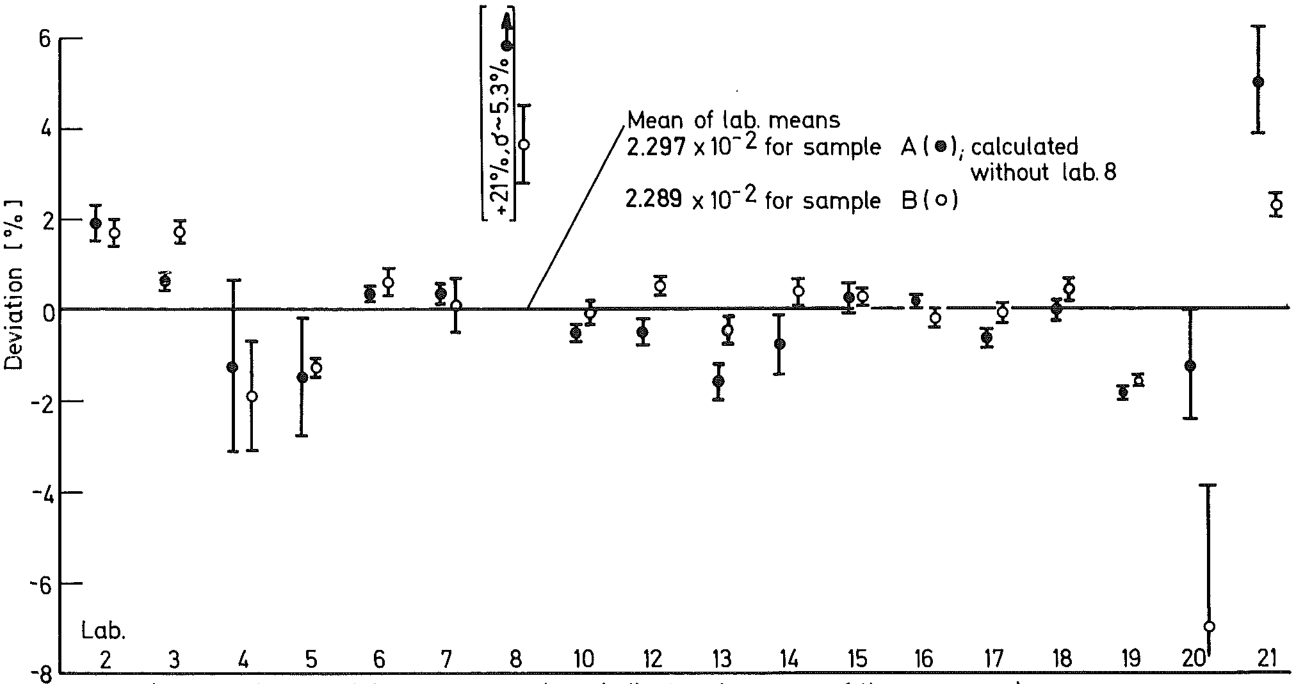
(Mean values per laboratory; error bars indicate ± 1σ-range of these means)

Fig.3-18 IDA-72: MS - Determinations of Isotopic Ratio Pu 241 / Pu 239 of Unspiked Samples A and B



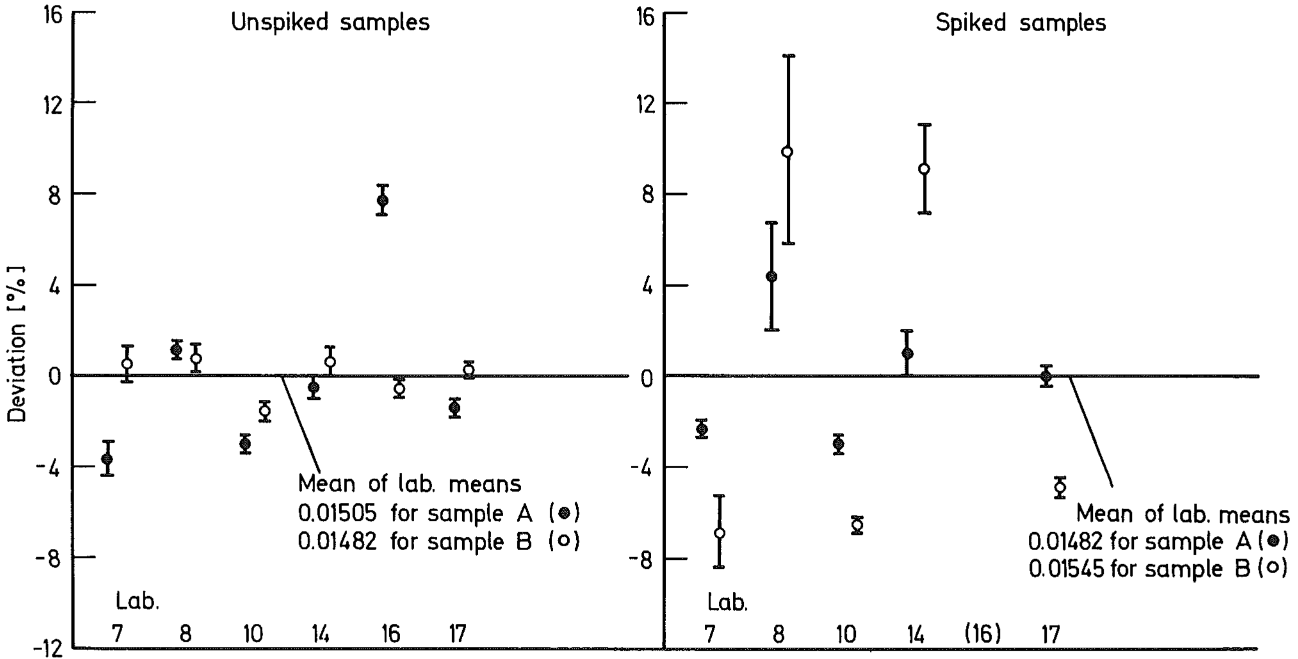
(Mean values per laboratory; error bars indicate ±1σ-range of these means)

Fig. 3-19 IDA-72: MS- Determinations of Isotopic Ratio Pu 241 / Pu 239 of Spiked Samples A and B



(Mean values per laboratory; error bars indicate ± 1σ-range of these means)

Fig.3-20 IDA-72: MS - Determinations of Isotopic Ratio Pu 242 / Pu 239 of Unspiked Samples A and B



(Mean values per laboratory; error bars indicate ± 1σ -range of these means)

Fig.3 - 21 IDA-72: MS-Determinations of Isotopic Ratio Pu 238 / Pu 239 of Unspiked and Spiked Samples A and B

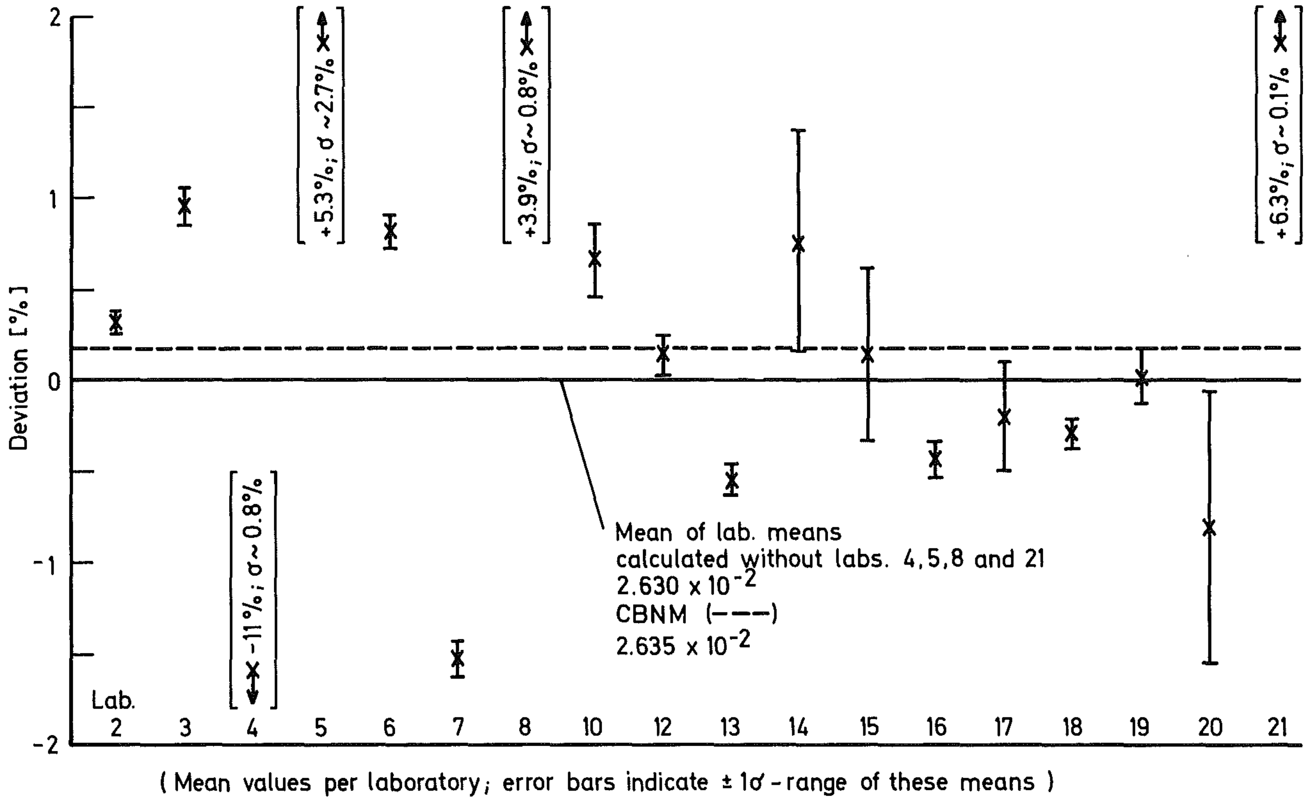


Fig. 3-22 IDA-72 : MS - Determinations of Isotopic Ratio Pu 240 / Pu 239 of Unspiked Sample R

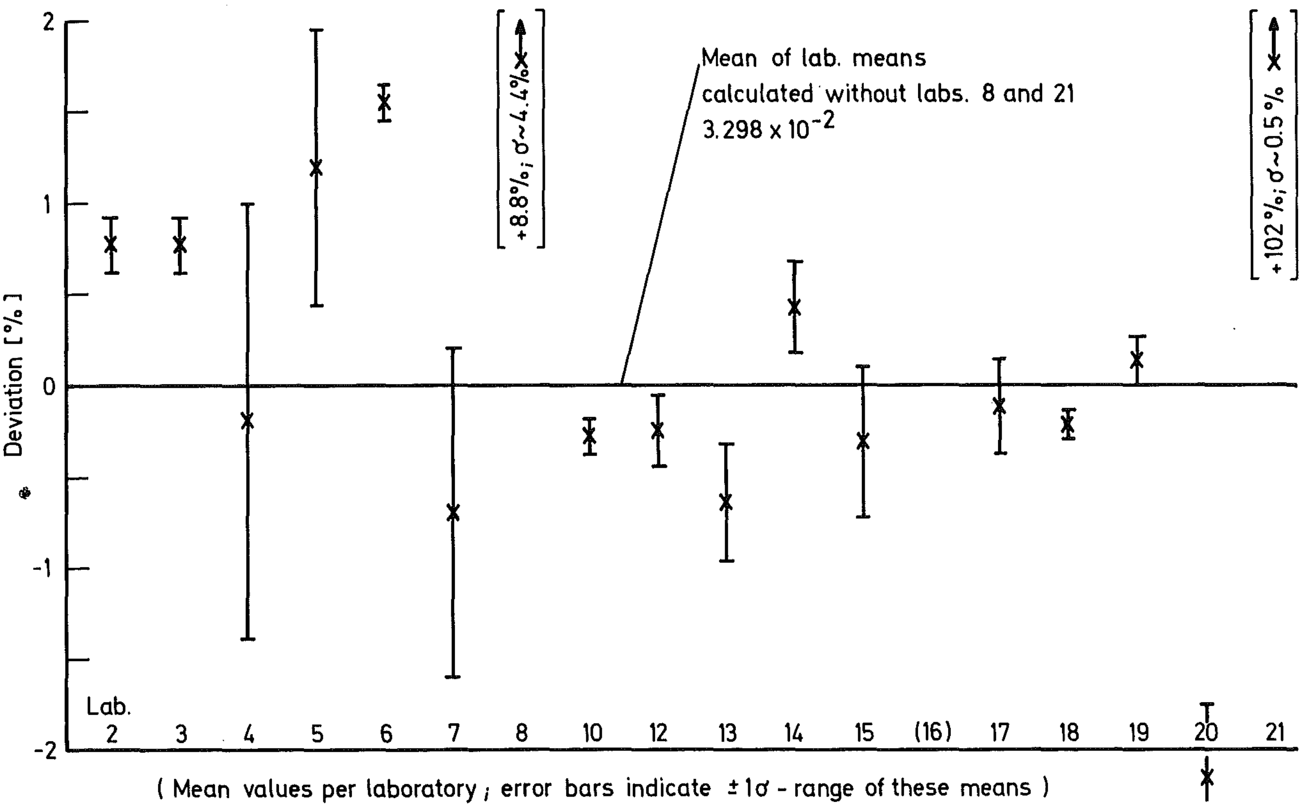
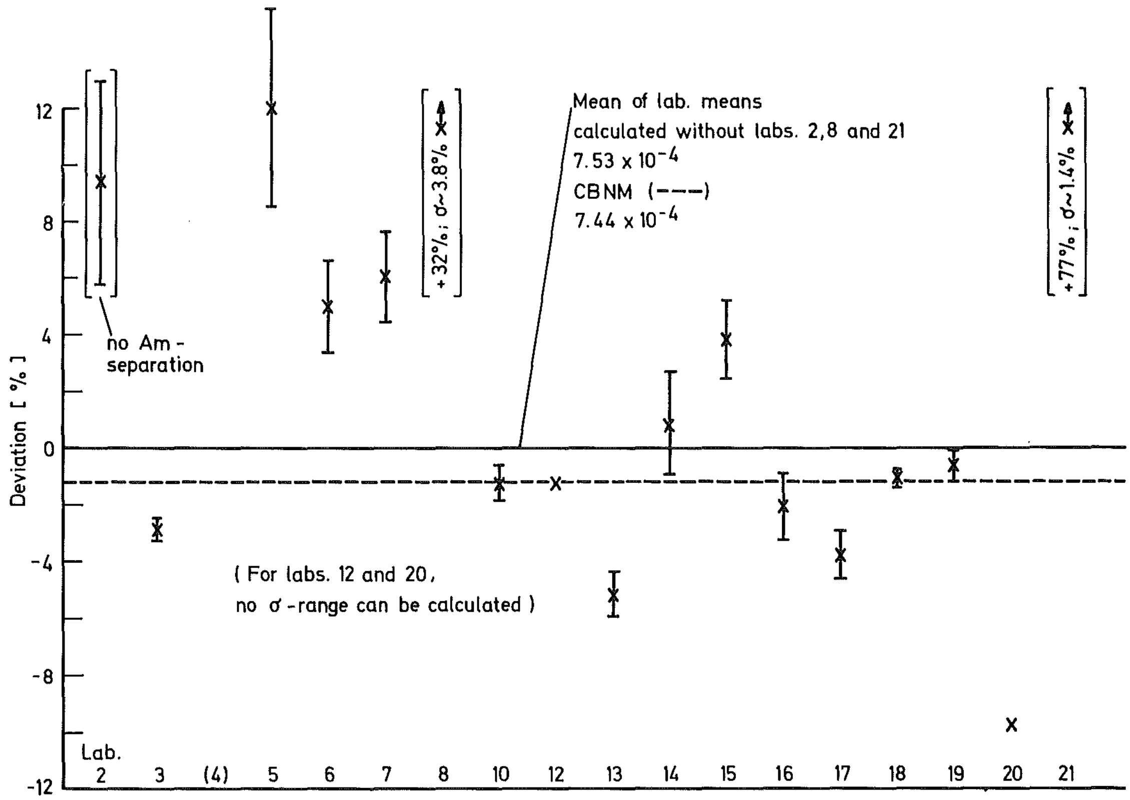
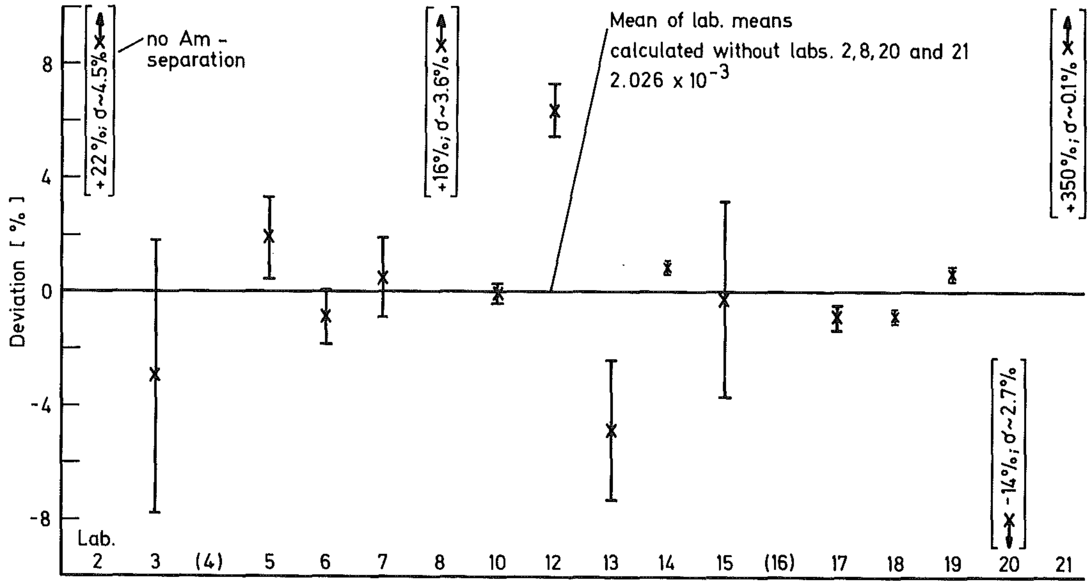


Fig. 3-23 IDA-72 : MS - Determinations of Isotopic Ratio Pu 240 / Pu 239 of Spiked Sample R



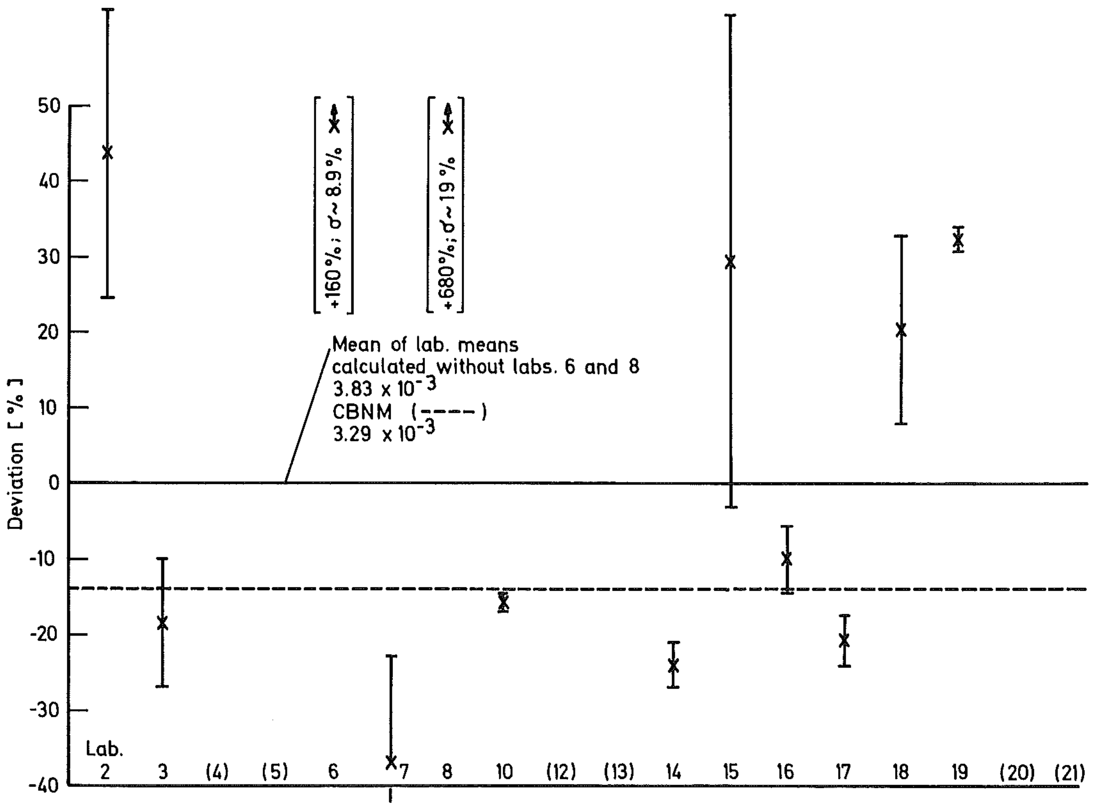
(Mean values per laboratory; error bars indicate ±1σ - range of these means)

Fig. 3-24 IDA-72: MS - Determinations of Isotopic Ratio Pu 241 / Pu 239 of Unspiked Sample R



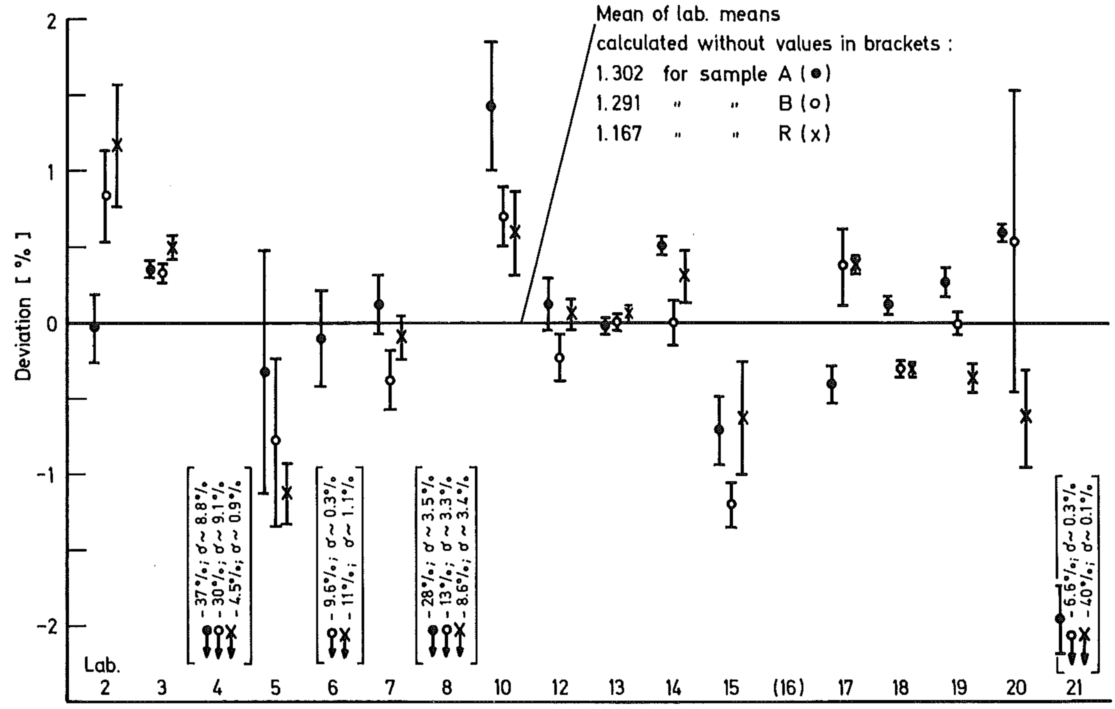
(Mean values per laboratory; error bars indicate ±1σ - range of these means)

Fig. 3-25 IDA-72: MS - Determinations of Isotopic Ratio Pu 241 / Pu 239 of Spiked Sample R



(Mean values per laboratory; error bars indicate ± 1σ-range of these means)

Fig. 3-26 IDA-72 : MS - Determinations of Isotopic Ratio Pu 242 / Pu 239 of Unspiked Sample R



(Mean values per laboratory ; error bars indicate ± 1σ-range of these means)

Fig. 3-27 IDA-72 : MS - Determinations of Isotopic Ratio Pu 242 / Pu 239 of Spiked Samples A, B and R

From the results shown in these figures, the following observations and statements can be made:

- In total, 29 of 361 laboratory mean values (8.0%) had to be considered as outliers. The highest rate of 20% (10 outliers out of 51 determinations) was found in the Pu-242/Pu-239 measurements of the spiked solutions /Fig. 3-27/. According to the opinion of the analysts /Par.8.3.1 and 8.5/, in the majority of the cases this is caused by insufficient valency adjustment between the Pu-VI in the spike and the Pu-IV in the sample due to unsuitable redox procedures. /Vol. II, Chapt. 6/.

  Besides this effect, cross contamination with plutonium of other isotopic composition explains the outlier values most likely, specificly for the ratios of other isotopes than Pu-242.

- As in the case of uranium, the mean values of the laboratory means, calculated for sample A and sample B after rejection of outliers, are in excellent agreement.

- The agreement between the calculated means of laboratory means and the values certified by CBNM is satisfactory, provoided that all suspect values are rejected. This comparison is possible for measurements on the single spike solution and the unspiked R-sample.

- As already observed for the measurements of uranium, in many cases the deviations of the values obtained for the A and B sample by the same laboratory on a certain isotopic ratio are clearly correlated, indicating a laboratory bias.

3.2.3 Calculation of Estimates for the Relative Standard Deviations of Error Components

For the measurements of all the uranium and plutonium isotopic ratios of the single spike solutions and the unspiked and spiked A, B and R samples analyses of variances were performed in order to get estimates for the different error components, contributing to the total error. The three error components considered were the scan, the run, and the interlaboratory component. An outline of the underlying structure of evaluation as it was executed for each sample and isotopic ratio is given in Par. 2.5.

The results are summarized in Tab. 3-1 for the uranium isotopic ratios and in Tab. 3-2 for the plutonium isotopic ratios. They are compiled in the sequence of decreasing values for the isotopic ratios, given in column 4 of the tables. The calculated estimates of the variances corresponding to the three error components are given in terms of relative standard deviations in columns 5 to 7. As these calculations are meaningful only under the condition that the expectation values for the variances in each step (scan, run or interlaboratory) are of the same order of magnitude, a number of measurements had to be omitted. They are indicated in the last columns of the tables. It should be noted that for this reason all evaluation results obtained by analysis of variances represent that group of laboratories only, which remains after the rejection of all types of outlier values.

In case of the isotope ratio Pu-238/Pu-239, many laboratories reported no mass spectrometric values as they preferred to use α-spectrometry for these measurements /Par. 3.3/.

For the graphical presentations of these results, which are given in Fig. 3-28 (uranium) and Fig. 3-29 (plutonium, mean values of the relative standard deviations corresponding to the error components were used. They were calculated for each group of data obtained from isotopic ratios of approximately the same value. In Tables 3-1 and 3-2 these groups are indicated by the horizontal lines.

Tab. 3-1: IDA-72: Results of the Analysis of Variances for the Mass Spectrometric Determination of Uranium Isotopic Ratios

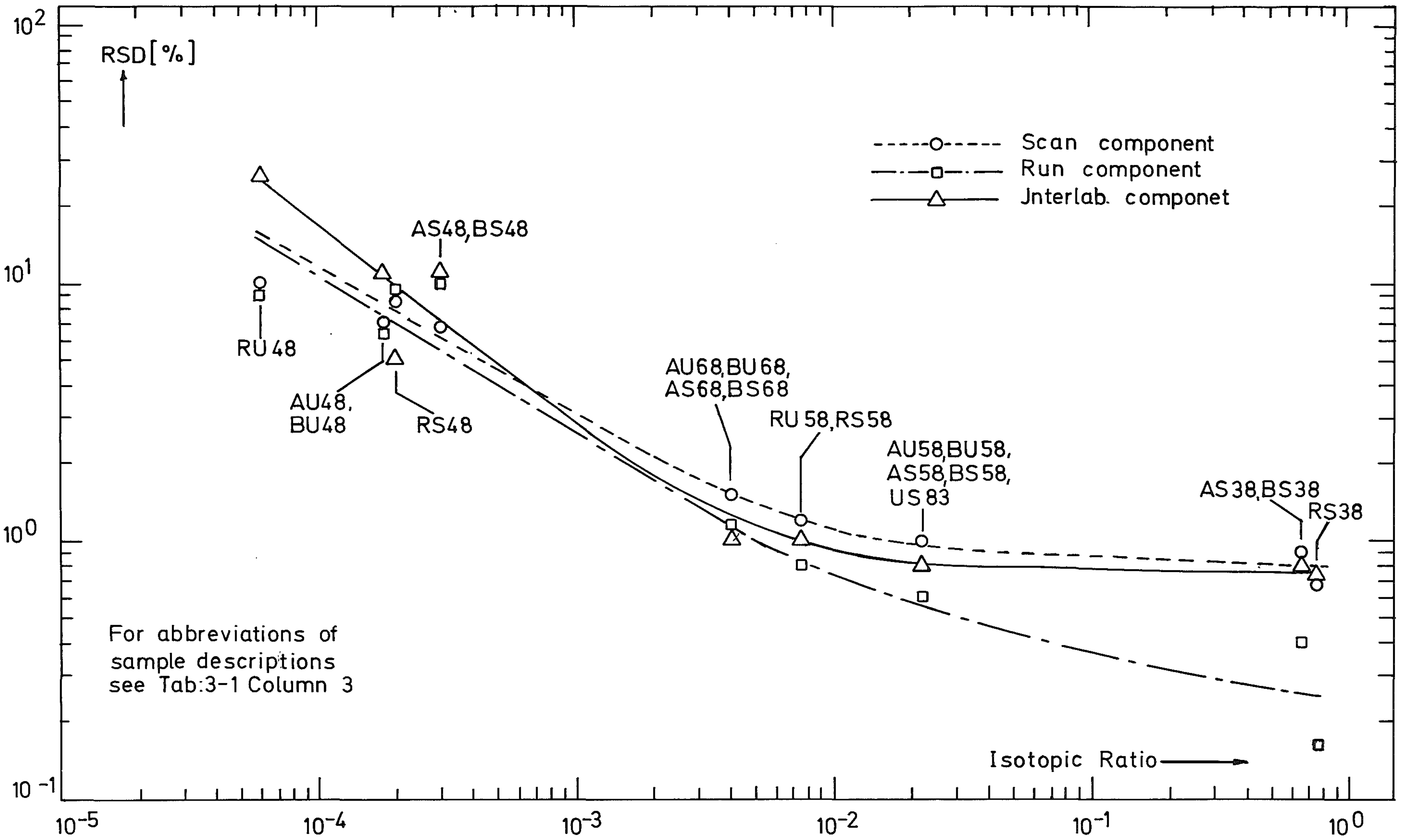
Sample	Isotopic ratio	Abbreviations in Fig. 3-28	Calculated mean of lab. means	Calculated estimates for the RSD [%]			Basis of calculation			Code No. of labs. which reported no data	Code No. of labs. omitted from calculation because		
				Scan component	Run Component	Interlab. Component	No. of labs.	No. of runs	No. of scans		lab. mean value is considered as outlier	of abnormally high RSD of lab. mean	only one scan value per run available
1	2	3	4	5	6	7	8	9	10	11	12	13	14
R spiked	233/238	RS 38	$7.53x10^{-1}$	0.68	0.16	0.71	18	54	432	16	-	-	-
A spiked	233/238	AS 38	$6.40x10^{-1}$	0.79	0.49	0.78	18	54	432	16	-	-	-
B spiked	233/238	BS 38	$6.33x10^{-1}$	1.00	0.28	0.81	18	54	432	16	-	-	-
A unspiked	235/238	AU 58	$2.23x10^{-2}$	0.91	0.45	0.81	19	57	456	-	-	-	-
B unspiked	235/238	BU 58	$2.22x10^{-2}$	0.95	0.72	0.65	19	57	456	-	-	-	-
A spiked	235/238	AS 58	$2.22x10^{-2}$	1.12	0.57	0.91	17	51	408	16.23	-	-	-
B spiked	235/238	BS 58	$2.22x10^{-2}$	1.17	0.80	0.68	17	51	408	16.23	-	-	-
U 233 spike	238/233	US 83	$2.21x10^{-2}$	0.77	0.44	0.96	15	45	360	-	5, 8, 20, 21	-	-
R unspiked	235/238	RU 58	$7.26x10^{-3}$	0.93	0.62	0.83	18	54	432	-	21	-	-
R spiked	235/238	RS 58	$7.51.10^{-3}$	1.44	1.06	1.13	16	48	384	16.23	21	-	-
A unspiked	236/238	AU 68	$3.93x10^{-3}$	1.57	1.15	1.00	17	51	407	23	4	-	-
B unspiked	236/238	BU 68	$3.93x10^{-3}$	1.37	1.28	1.44	17	51	404	23	-	18	-
A spiked	236/238	AS 68	$3.89x10^{-3}$	1.61	1.23	0.56	14	42	336	16.23	20	4.18	-
B spiked	236/238	BS 68	$3.88x10^{-3}$	1.52	0.89	1.08	14	42	336	16.23	4, 18, 20	-	-
A spiked	234/238	AS 48	$2.92x10^{-4}$	7.89	10.4	11.5	12	36	288	4,12,16,18,21,23	-	20	-
B spiked	234/238	BS 48	$3.02x10^{-4}$	5.72	10.1	10.7	13	37	296	4,12,16,18,21,23	-	-	-
R spiked	234/238	RS 48	$2.07x10^{-4}$	8.87	8.95	5.11	11	33	264	4,12,16,18,19,23	7	20	-
A unspiked	234/238	AU 48	$1.79x10^{-4}$	7.71	7.93	14.0	15	45	359	4,12,21,23	-	-	-
B unspiked	234/238	BU 48	$1.72x10^{-4}$	6.29	4.54	8.40	15	45	356	4,12,21,23	-	-	-
R unspiked	234/238	RU 48	$5.96x10^{-5}$	10.2	9.06	25.8	12	36	288	4,13,16,21,23	5	-	12

Tab. 3-2: IDA-72: Results of the Analysis of Variances for the Mass Spectrometric Determination of Plutonium Isotopic Ratios

Sample	Isotopic ratio	Abbreviations in Fig. 3-28	Calculated mean of lab means	Calculated estimates for the RSD [%]			Basis of calculation			Code No. of labs. which reported no data	Code No. of labs. omitted from calculation because		
				Scan Component	Run Component	Interlab. Component	No. of labs.	No. of runs	No. of scans		lab. mean value is considered as outlier	of abnormally high RSD of lab. mean	of other reasons
1	2	3	4	5	6	7	8	9	10	11	12	13	14
A spiked	242/239	AS 29	1.30×10^{0}	0.74	0.41	0.68	15	45	360	16	4,8	-	-
B spiked	242/239	BS 29	1.29×10^{0}	0.59	0.61	0.45	13	39	312	16	4,6,8,21	-	-
R spiked	242/239	RS 29	1.17×10^{0}	0.65	0.29	0.58	13	39	312	16	4,6,8,21	-	-
A unspiked	240/239	AU 09	2.31×10^{-1}	0.66	0.20	0.23	16	48	384	-	-	4,5	-
B unspiked	240/239	BU 09	2.30×10^{-1}	0.67	0.12	0.37	18	54	432	-	-	-	-
A spiked	240/239	AS 09	2.34×10^{-1}	1.00	0.45	0.59	17	51	408	16	-	-	-
B spiked	240/239	BS 09	2.34×10^{-1}	1.08	0.41	0.43	16	48	384	16	-	20	-
A unspiked	241/239	AU 19	1.27×10^{-1}	1.05	0.60	0.73	17	51	408	-	-	-	2[1]
B unspiked	241/239	BU 19	1.27×10^{-1}	0.92	0.14	0.40	17	51	408	-	-	-	2[1]
A spiked	241/239	AS 19	1.27×10^{-1}	1.56	0.56	0.66	16	48	384	16	-	-	2[1]
B spiked	241/239	BS 19	1.26×10^{-1}	1.25	0.75	0.40	15	45	360	16	-	20	2[1]
R spiked	240/239	RS 09	3.30×10^{-2}	0.85	0.78	0.75	15	45	360	16	8,21	-	-
R unspiked	240/239	RU 09	2.63×10^{-2}	0.83	0.46	0.62	14	42	336	-	4,5,8,21	-	-
A unspiked	242/239	AU 29	2.30×10^{-2}	1.46	1.19	1.48	17	51	408	-	8	-	-
B unspiked	242/239	BU 29	2.29×10^{-2}	1.64	1.28	2.04	18	54	432	-	-	-	-
A unspiked	238/239	AU 89	1.51×10^{-2}	1.55	0.61	4.17	6	18	144	2,3,4,5,6,12,13	-	-	-
B unspiked	238/239	BU 89	1.48×10^{-2}	1.43	0.55	0.85	6	18	144	15,18,19,20,21	-	-	-
A spiked	238/239	AU 89	1.48×10^{-2}	2.83	1.85	2.57	5	15	120	2,3,4,5,6,12,13	-	-	-
B spiked	238/239	BS 89	1.55×10^{-2}	2.71	4.07	8.24	5	15	120	15,16,18,19,20,21	-	-	-
R spiked	241/239	RS 19	2.03×10^{-3}	3.22	3.16	1.90	12	36	288	4,16	8,20,21	-	2[1]
Pu 242 spike	240/242	PS 02	8.35×10^{-4}	3.08	0.77	3.02	14	41	328	-	8,16,21	-	12[2]
R unspiked	241/239	RU 19	7.60×10^{-4}	3.70	2.32	4.66	12	36	288	4	8,21	-	2[1], 12[2], 20[2]
Pu 242 spike	239/242	PS 92	2.19×10^{-4}	8.13	4.09	18.9	15	42	336	-	16,21	-	12[2]
R unspiked	242/239	RU 29	3.83×10^{-5}	13.5	29.4	22.7	10	30	240	4,5,12,13,20,21	6,8	-	-

1) N_o Am-separation performed

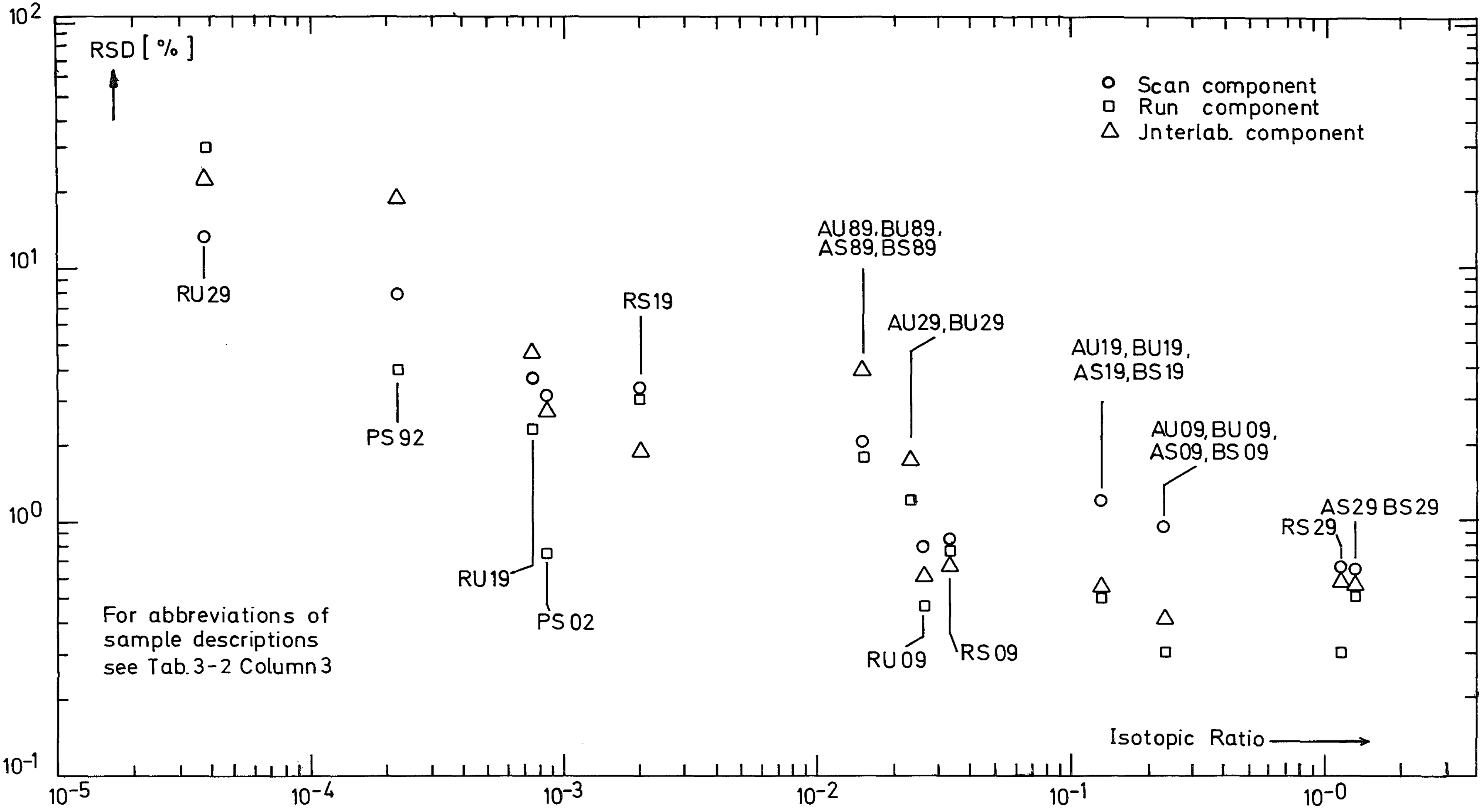
2) only one scan value per run available



For abbreviations of sample descriptions see Tab:3-1 Column 3

(Calculated after rejection of ~ 9 % of the basic values as outliers; see Tab. 3-1)

Fig. 3-28 IDA-72: Estimates for the Relative Standard Deviations of the Error Components in the MS-Determination of Uranium Isotopic Ratios



(Calculated after rejection of ~5 % of the basic values as outliers; see Tab. 3-2)

Fig. 3-29 IDA-72: Estimates for the Relative Standard Deviations of the Error Components in the MS-Determination of Plutonium Isotopic Ratios

In the case of plutonium /Fig. 3-29/, no meaningful curves could be drawn because of the wide spread of the calculated points. Nevertheless, as appears from the figures, all the three error components considered are of the same order of magnitude and increase markedly with decreasing isotopic ratio. This means that the interlaboratory component contributes the main part to the total error of isotopic ratio determinations, as the influences of the run and scan components are usually reduced by repetition measurements. 1)

As already discussed /Par. 3.1/, errors of the sample preparation steps before filament loading should only become visible in the isotopic ratios U-233/U-238 and Pu-242/Pu-239 of the spiked samples. In the case of plutonium, such effects were indead found /Fig. 3-27 and Par. 3.2.2/ but are not reflected by the results of the variance analysis, as the values concerned had to be rejected as outliers. On the other hand, comparison of the values calculated for the run component of other isotopic ratios of plutonium /Tab. 3-2, column 6/ indicates somewhat higher values for spiked than for unspiked material. This may be caused by the small Pu-239 content of the mixed spike solution /Tab. 2-1 / due to the plutonium impurity in the U-233 spike material. Therefore, this effect should not be considered as a proof for higher run component values of spiked samples in general.

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1) The relative standard deviation associated in average to the result of an isotopic ratio determination carried out in ℓ laboratories, each one performing s runs of n scans, is given by

$$\delta = \left(\frac{1}{\ell}\,\delta^2_{\text{interlaboratory}} + \frac{1}{\ell s}\,\delta^2_{\text{run}} + \frac{1}{\ell s n}\,\delta^2_{\text{scan}} \right)^{\frac{1}{2}}$$

with $\delta_{\text{interlaboratory}}$, δ_{run} and δ_{scan} being the relative standard deviations for the error components calculated in this paragraph.

3.3 Determination of Pu-238

3.3.1 Participation

The laboratories determined the Pu-238 content of the samples a follows:

by α-spectrometry only:	8 laboratories
by mass-spectrometry only:	4 "
using both methods:	3 "

The laboratories 2, 12 and 20 reported no data.

3.3.2 α -Spectrometric Determination

A survey on the measurement techniques used by the laboratories is given in Volume II, Chapt.8/.

Each laboratory reported three single values of the α-activity ratio Pu-238/(Pu-239 + Pu-240) obtained on the spiked and unspiked samples A, B and R with the exception of Lab. 21, which reported one single determination per sample only. In Tab. 3-3 to Tab. 3-5 the means of these three values ("lab. means"), the relative standard deviations (RSD) of the single determinations and the corresponding isotopic ratios Pu-238/Pu-239 are compiled. The isotopic ratio was calculated according to

$$R\ (238/239) = \tau(238) \cdot \alpha(238/(239+240)) \cdot \left(\frac{1}{\tau(239)} + \frac{R\ (240/239)}{\tau(240)}\right)$$

with $\alpha(238/(239+240))$ ≙ the laboratory mean value of the α-spectrometric determination,

$R\ (240/239)$ ≙ the laboratory mean value of the mass-spectrometric determination of this isotopic ratio,

and the half life values τ /Vol. II, Par. 1.3/ .

$\tau\ (238) = 87.7$ years

$\tau\ (239) = 2.44 \times 10^4$ years

$\tau\ (240) = 6.58 \times 10^3$ years

Table 3-3: IDA-72 : α - Spectrometric Determination of Pu-238 on Unspiked Samples A and B

Laboratory Code	Sample A, unspiked			Sample B, unspiked		
	Lab.mean of α-activity ratio $\frac{\text{Pu-238}}{\text{(Pu-239+Pu-240)}}$	RSD of single determination [%]	Calculated isotopic ratio $\frac{\text{Pu-238}}{\text{Pu-239}}$	Lab.mean of α-activity ratio $\frac{\text{Pu-238}}{\text{(Pu-239+Pu-240)}}$	RSD of single determination [%]	Calculated isotopic ratio $\frac{\text{Pu-238}}{\text{Pu-239}}$
3	2.194	1.01	0.01466	2.193	1.39	0.01462
4	2.153	2.18	0.01435	2.169	1.31	0.01443
5	2.182	0.74	0.01455	(1.798)	0.54	(0.01199)
6	2.213	1.55	0.01477	2.192	1.07	0.01462
7	2.180	1.47	0.01454	2.184	0.05	0.01454
13	2.206	0.73	0.01470	2.188	0.43	0.01457
15	2.203	0.17	0.01470	2.218	2.26	0.01478
17	2.204	0.52	0.01470	2.196	0.23	0.01465
18	2.193	0.70	0.01462	2.137	0.71	0.01424
19	2.213	0.29	0.01474	2.208	0.39	0.01470
21	(1.366)	-	(0.00911)	(1.494)	-	(0.00996)
Mean of lab. means	2.194	-	0.01463	2.187	-	0.01457

Values in brackets are considered as outliers and not used for calculating the mean of lab. means.

Table 3-4: IDA-72 : α -Spectrometric Determination of Pu-238 on Spiked Samples A and B

Laboratory Code	Sample A, spiked			Sample B, spiked		
	Lab. mean of α -activity ratio $\frac{\text{Pu-238}}{\text{(Pu-239+Pu-240)}}$	RSD of single determination [%]	Calculated isotopic ratio $\frac{\text{Pu-238}}{\text{Pu-239}}$	Lab. mean of α-activity ratio $\frac{\text{Pu-238}}{\text{(Pu-239+Pu-240)}}$	RSD of single determination [%]	Calculated isotopic ratio $\frac{\text{Pu-238}}{\text{Pu-239}}$
3	2.134	1.46	0.01436	2.146	1.00	0.01448
4	2.113	1.56	0.01404	2.085	1.96	0.01402
5	2.059	0.43	0.01382	2.134	1.06	0.01431
6	2.162	0.55	0.01455	2.156	0.50	0.01446
7	2.162	0.35	0.01455	2.158	0.03	0.01445
13	2.163	1.08	0.01451	2.126	0.17	0.01427
15	2.164	2.98	0.01452	2.172	3.48	0.01454
17	2.175	0.23	0.01463	2.177	0.12	0.01463
18	2.153	1.42	0.01446	2.140	0.47	0.01435
19	2.167	0.61	0.01458	2.160	0.13	0.01453
21	(1.045)	-	(0.00702)	(0.884)	-	(0.00594)
Mean of lab. means	2.145	-	0.01440	2.145	-	0.01440

Values in brackets are considered as outliers and not used for calculating the mean of lab. means.

Table 3-5: IDA-72 : α-Spectrometric Determination of Pu-238 on R-Samples

Laboratory Code	Sample R, unspiked			Sample R, spiked		
	Lab. mean of α-activity ratio $\frac{\text{Pu-238}}{\text{(Pu-239+Pu-240)}}$	RSD of single determination [%]	Calculated isotopic ratio $\frac{\text{Pu-238}}{\text{Pu-239}}$	Lab. mean of α-activity ratio $\frac{\text{Pu-238}}{\text{(Pu-239+Pu-240)}}$	RSD of single determination [%]	Calculated isotopic ratio $\frac{\text{Pu-238}}{\text{Pu-239}}$
3	0.0101	4.89	0.00004	0.0235	2.80	0.00010
4	0.0100	6.26	0.00004	0.0197	4.33	0.00008
5	0.0093	4.69	0.00004	(0.0717)	0.58	(0.00029)
6	0.0173 1)	6.97	0.00007	0.0218	7.99	0.00009
7	0.0097	1.58	0.00004	0.0229	6.62	0.00009
13	0.0197	1.40	0.00008	(0.0461)	1.95	(0.00019)
15	0.0101	3.42	0.00004	-	-	-
17	0.0098	0.59	0.00004	0.0294	1.10	0.00012
18	0.0094	3.35	0.00004	0.0286	2.62	0.00012
19	-	-	-	-	-	-
21	(0.0674)	-	(0.00027)	(0.1053)	-	(0.00047)
Mean of lab. means	0.0117	-	0.00005	0.0243	-	0.00010

Values in brackets are considered as outliers and not used for calculating the mean of lab. means.

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1) Mean value of 2 single determinations only. The third determination was marked as outlier by the laboratory.

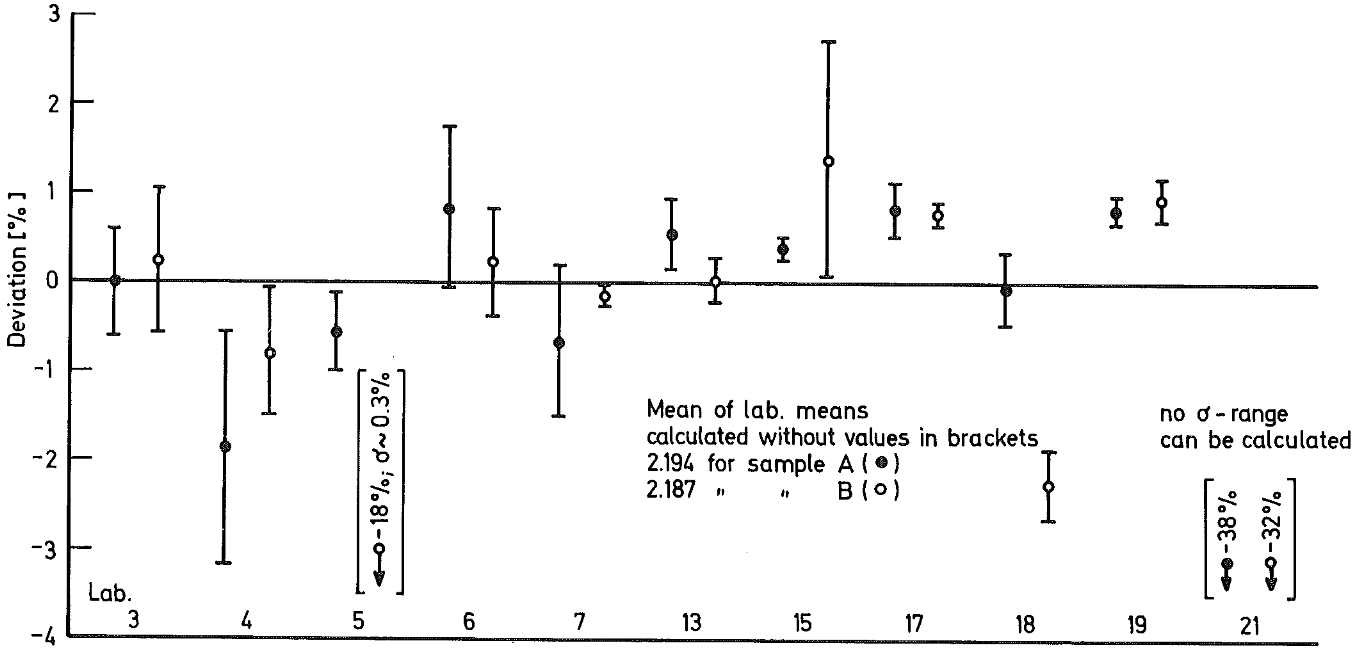
The laboratory mean values of the α-activity ratios with indication of their relative standard deviations are shown

- in Fig. 3-30 and Fig. 3-31 for the unspiked and spiked samples A and B,
- in Fig. 3-32 and Fig. 3-33 for the unspiked and spiked R-sample.

All measurements of laboratory 21 had to be considered as outliers, very probably caused by cross contamination. As only one determination per sample was reported, no standard deviations could be calculated.

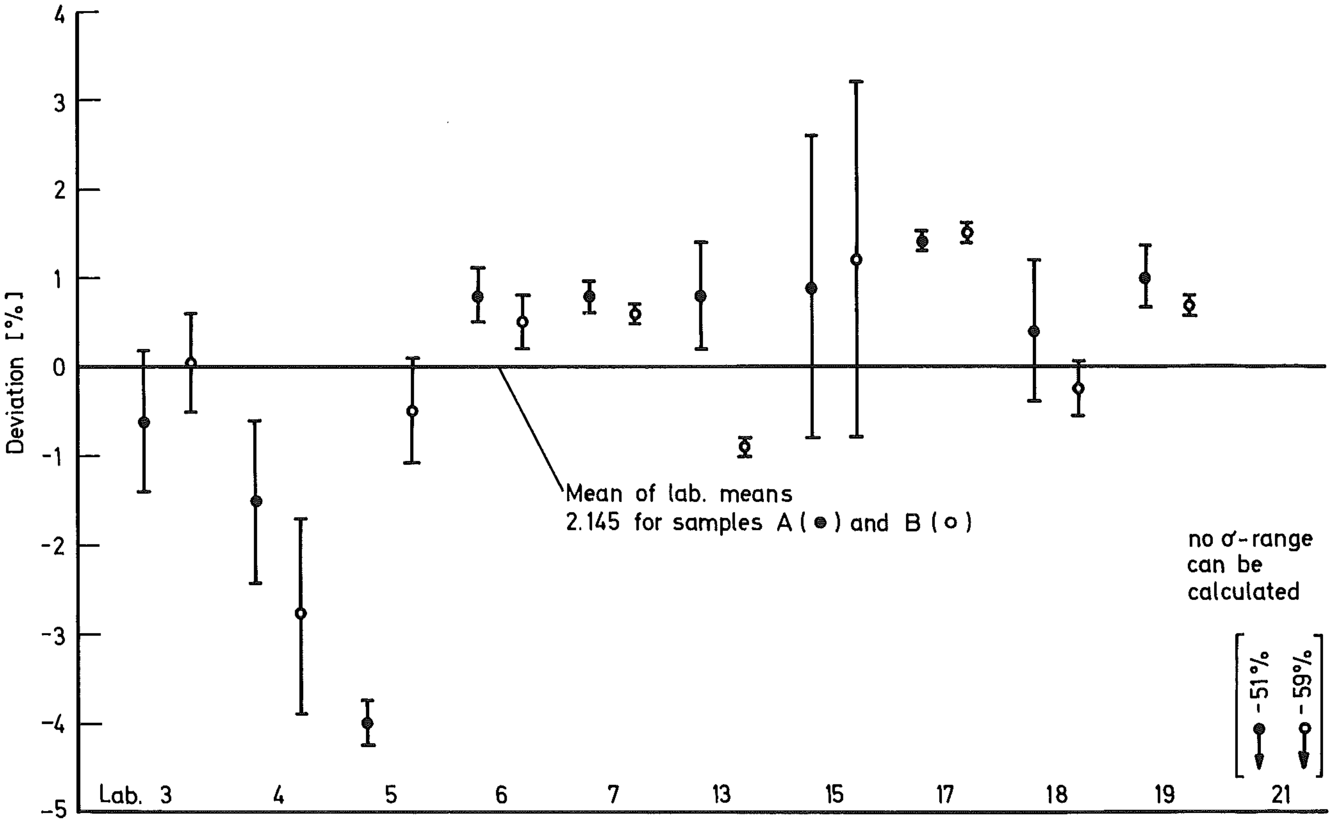
In case of the three further outlier values indicated /Tab. 3-3; 3-5 and Fig. 3-30; 3-33/ it should be noted that they could not be detected by the laboratories themselves, as the relative standard deviations were normal. Their identification as outliers became possible only by comparison with the results of the other laboratories.

Concerning the determinations on the unspiked R-sample by the laboratories 6 and 13 /Fig. 3-32/, it is doubtful whether or not they should be considered as outliers. Therefore, the means of the laboratory means both with and without these measurements, were given in the figure.



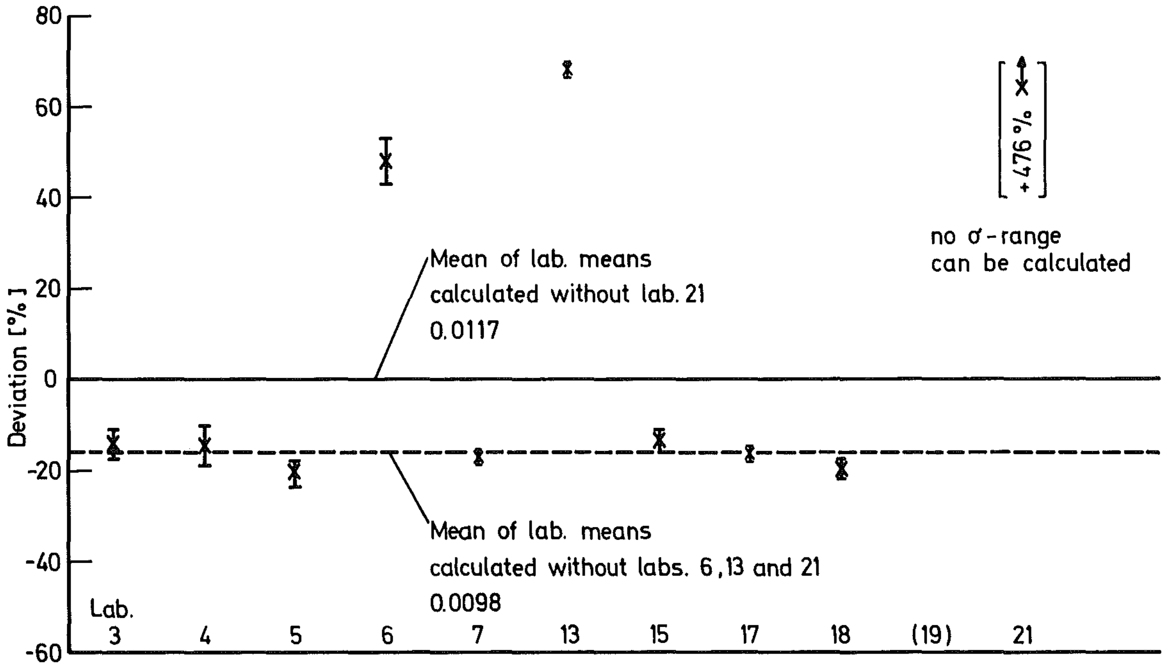
(Mean values per laboratory; error bars indicate ±1σ-range of these means)

Fig.3-30 IDA-72: α-Spectrometric Determinations of the Activity Ratio
Pu 238 / (Pu 239 + Pu 240) on the Unspiked Samples A and B



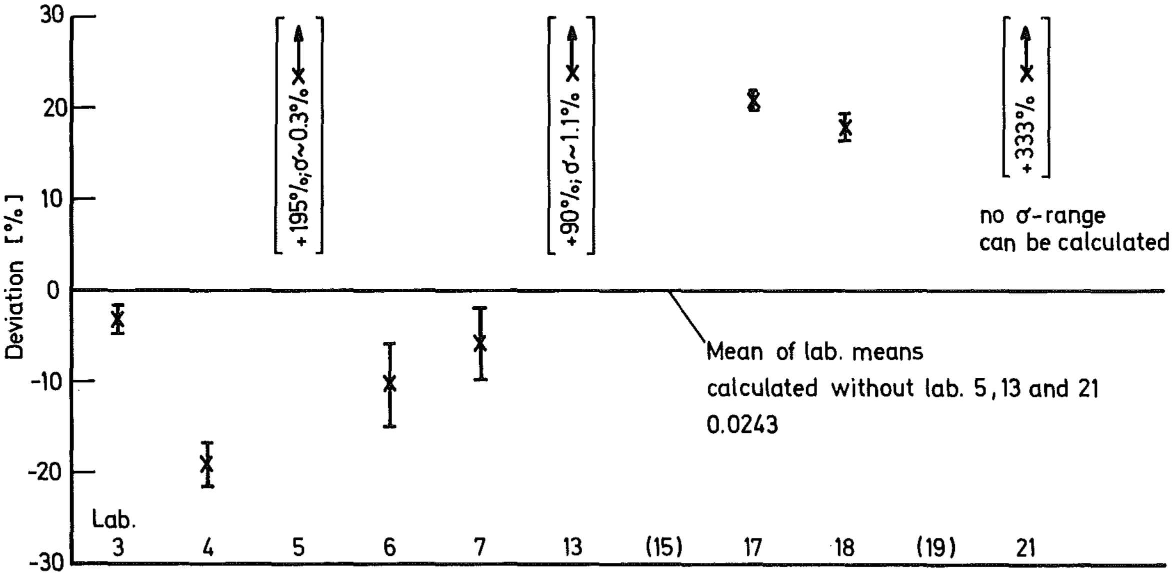
(Mean values per laboratory; error bars indicate ± 1σ-range of these means)

Fig.3-31 IDA-72: α-Spectrometric Determinations of the Activity Ratio
Pu 238 / (Pu 239 + Pu 240) on the Spiked Samples A and B



(Mean values per laboratory; error bars indicate ± 1σ-range of these means)

Fig. 3-32 IDA-72: α-Spectrometric Determinations of the Activity Ratio Pu 238 / (Pu 239 + Pu 240) on the Unspiked Sample R



(Mean values per laboratory; error bars indicate ± 1σ-range of these means)

Fig. 3-33 IDA-72: α-Spectrometric Determinations of the Activity Ratio Pu 238 / (Pu 239 + Pu 240) on the Spiked Sample R

According to the layout of the standard experiment, there should be no difference in the relative Pu-238 content of the unspiked A and B samples. This is confirmed by the nearly indentical values of the mean of the laboratory means calculated in Tab. 3-3 . From these data, 2.191 and 0.01460 can be considered as the "best" values obtained in this experiment for the α-activity ratio Pu-238/(Pu-239 + Pu-240) and the isotopic ratio Pu-238/Pu-239 of the unspiked samples A and B. The corresponding values of the spiked samples /Tab. 3-4/ - for which, again, no significant difference between A and B does exist - are somewhat lower with 2.145 and 0.01440, respectively, because of the small amounts of Pu-239 contained in the mixed spike solution /Tab.2-1/. For the same reason, there is a considerable difference in the Pu-238 content of the spiked and unspiked R-sample /Tab. 3-5/.

Analyses of variances were made to calculate the estimate values of the precision and the interlaboratory deviation for the four groups of α-spectrometric determinations belonging each to the same mean value, i.e.

unspiked A and B samples,
spiked A and B "
unspiked R sample,
spiked R " .

The results are compiled in Tab. 3-6 in the order of decreasing values for the α-activity ratio. The differences in the values calculated for the spiked and unspiked A and B-samples indicate the variance of these values themselves. Furthermore, it is clearly shown that mainly the interlaboratory deviation increases considerably with decreasing Pu-238 content. The strong dependence of the calculated figures on the question whether or not deviating single results are considered as outliers is demonstrated in the case of the unspiked R sample:

As shown by Fig. 3-32, one could also decide to consider the results of the laboratories 6 and 13 as outliers, which would reduce the calculated interlaboratory deviation by a factor of 10, approximately /Tab. 3-6/.

Table 3-6: IDA-72: Calculated RSD of Error Components for the α-Spectrometric Determinations of the Activity Ratio Pu-238/(Pu-239 + Pu-240).

Sample	Mean of lab. means obtained for α-activity ratio $\frac{\text{Pu-238}}{\text{(Pu-239+Pu-240)}}$	Calculated isotopic ratio Pu-238/Pu-239	Precision RSD [%]	Interlab. deviation RSD [%]	Number of labs. contributing to these calculations	Total of single determinations on which calculations are based
A and B, unspiked	2.191	0.01460	1.13	0.66	10	57
A and B, spiked	2.145	0.01440	1.41	1.14	10	60
R spiked	0.0243	0.00010	4.49	15.7	6	18
R [1] unspiked	0.0117 (0.0098)	0.00005 (0.00004)	4.08 (3.96)	33.1 (2.29)	9 (7)	26 (21)

[1] Values in brackets are obtained if results of laboratory 6 and 13 are also considered as outliers.

3.3.3 Mass Spectrometric Determination

The mass spectrometric determinations of the isotopic ratio Pu-238/Pu-239 were reported and evaluated in the same way as the other isotopic ratios /Par. 3.2.2/. The laboratory mean values obtained on the spiked and unspiked samples A, B and R are compiled in Tables 3-7 to 3-9, together with the relative standard deviations of the scan and run error component. The results obtained on the A and B samples are also shown in Fig. 3-34 which is identical with Fig. 3-21, already given in Par. 3.2.2.
Because of the limited number of data available, the measurements on the R-samples were not further evaluated. Comparison with the results of the α-spectrometric determination /Tab. 3-5/ shows for this very low isotopic ratio at least some agreement in a few cases.

For the measurements on the spiked samples A and B as well as for the unspiked ones, analyses of variances were performed based on the run mean values 1). The estimates for the precision and interlaboratory deviation calculated in this way are compiled in Tab. 3-10 and compared with the results obtained by α-spectrometry.

Although there is rather good agreement in the mean values of the isotopic ratios, the calculated estimates for precision and interlaboratory deviation indicate that α-spectrometry is superior in general in this concentration range.

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1) By this way of calculation, the "precision" represents mainly the run component, slightly enlarged by contributions of the scan component.

Table 3-7: IDA-72: Mass Spectrometric Determination of Pu-238 on Unspiked Samples A and B

Laboratory Code	Sample A, unspiked			Sample B, unspiked		
	Lab. mean of isotopic ratio $\frac{\text{Pu-238}}{\text{Pu-239}}$	RSD of scan component [%]	RSD of run component [%]	Lab. mean of isotopic ratio $\frac{\text{Pu-238}}{\text{Pu-239}}$	RSD of scan component [%]	RSD of run component [%]
7	0.01448	1.83	1.25	0.01490	1.67	1.12
8	0.01522	3.16	n.s. 1)	0.01494	2.85	0.21
10	0.01459	0.41	0.37	0.01459	0.52	0.39
14	0.01497	0.45	0.68	0.01494	0.46	0.59
16	0.01622	0.56	1.00	0.01471	0.34	0.20
17	0.01480	0.60	0.47	0.01486	0.82	n.s. 1)
Mean of lab.means	0.01505	-	-	0.01482	-	-

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1) n.s. means "not significant".

Table 3-8: IDA-72: Mass Spectrometric Determination of Pu-238 on Spiked Samples A and B

Laboratory Code	Sample A, spiked			Sample B, spiked		
	Lab. mean of isotopic ratio $\frac{\text{Pu-238}}{\text{Pu-239}}$	RSD of scan component [%]	RSD of run component [%]	Lab. mean of istopic ratio $\frac{\text{Pu-238}}{\text{Pu-239}}$	RSD of scan component [%]	RSD of run component [%]
7	0.01452	1.35	n.s. 1)	0.01440	1.21	2.75
8	0.01545	5.82	3.58	0.01697	5.30	7.07
10	0.01437	0.88	0.30	0.01443	0.67	n.s. 1)
14	0.01497	0.53	1.75	0.01684	0.87	3.65
16	-	-	-	-	-	-
17	0.01480	0.63	0.27	0.01463	0.61	0.48
Mean of lab.means	0.01482			0.01545		

Table 3-9: IDA-72: Mass Spectrometric Determination of Pu-238 on R-Sample

Laboratory Code	Sample R, unspiked			Sample R, spiked		
	Lab. mean of isotopic ratio $\frac{\text{Pu-238}}{\text{Pu-239}}$	RSD of scan component [%]	RSD of run component [%]	Lab. mean of isotopic ratio $\frac{\text{Pu-238}}{\text{Pu-239}}$	RSD of scan component [%]	RSD of run component [%]
7	-	-	-	-	-	-
8	0.000300 [1]	-	-	0.00144	33.0	83.1
10	0.000072	4.89	2.09	0.000083	4.85	2.07
14	0.000096	6.74	12.3	0.000154	3.98	18.3
16	-	-	-	-	-	-
17	0.000044	6.27	27.6	0.000219	11.0	41.2

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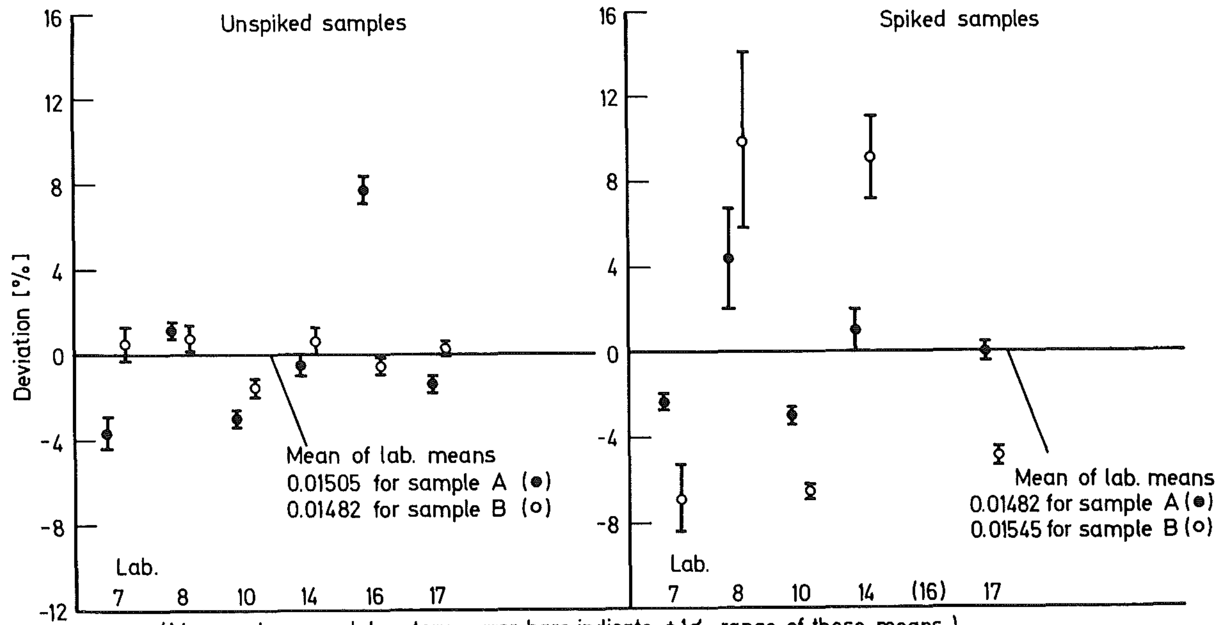
[1] Value reported as upper limit.



(Mean values per laboratory; error bars indicate ± 1σ-range of these means)

Fig. 3-34 IDA-72: MS-Determinations of Isotopic Ratio Pu 238 / Pu 239 of Unspiked and Spiked Samples A and B

Table 3-10: IDA-72: Calculated RSD of Error Components for the Mass Spectrometric Determination of the Isotopic Ratio Pu-238/Pu-239

Sample	Mean of lab. means for isotopic ratio Pu-238/Pu-239	Precision RSD [%]	Interlab. deviation RSD [%]	Number of labs. contributing to the calculations	Total number of run mean values on which calculations are based
A and B, unspiked	0.0149 (0.0146)	2.48 (1.13)	1.84 (0.66)	6	36
A and B, spiked	0.0151 (0.0144)	4.93 (1.41)	5.26 (1.14)	5	30

For comparison, data of the α-spectrometric determinations from Table 3-6 are given in brackets.

3.4 Calculated Isotopic Compositions

3.4.1 Uranium

The calculated isotopic compositions of the unspiked samples A, B and R are compiled in Tables 3-11 to 3-13. At the foot of the tables the calculated means of the laboratory means and the standard deviations and relative standard deviations of the laboratory mean values are given.

The data of laboratory 4 for sample A and of laboratory 21 for sample R were excluded from this calculation because they are considered as outliers /Fig. 3-6, Fig. 3-10 and Fig. 3-11/. Also the values of laboratory 23 for samples A and B were not taken into consideration as the abundance of the isotope U-236 was not measured, influencing the values for the other isotopes significantly.

The calculated mean values for the isotopic composition of the unspiked samples A and B are in very good agreement with each other, and so are the calculated mean value of the unspiked R-sample and the composition stated by CBNM for this solution, given at the foot of Tab. 3-13.

Table 3-11: IDA-72: Calculated Laboratory Mean Values of the Isotopic Composition of Sample A(unspiked)

Relative Isotopic Abundances [atom %]

Lab. Code	U-233	U-234	U-235	U-236	U-238
2	0.00008	0.0162	2.162	0.3818	97.440
3	-	0.0173	2.178	0.3919	97.413
4	-	-	(2.177)	(0.5125)	(97.311)
5	-	0.0247	2.195	0.3912	97.390
6	-	0.0167	2.179	0.3849	97.419
7	-	0.0135	2.145	0.3797	97.462
3	0.00657	0.0188	2.204	0.3766	97.394
10	0.00022	0.0162	2.155	0.3829	97.446
12	-	-	2.169	0.3866	97.444
13	-	0.0180	2.165	0.3805	97.436
14	-	0.0195	2.156	0.3833	97.441
15	-	0.0166	2.181	0.3861	97.416
16	-	0.0178	2.174	0.3817	97.427
17	-	0.0154	2.152	0.3808	97.452
18	-	0.0189	2.173	0.3746	97.433
19	-	0.0171	2.148	0.3820	97.453
20	-	0.0148	2.141	0.3770	97.468
21	-	-	2.165	0.3862	97.449
23	-	-	(2.212)	-	(97.788)
Mean of means:		0.0174	2.167	0.3828	97.434
SD		0.0026	0.017	0.0047	0.022
RSD [%]		14.7	0.79	1.23	0.02

Values in brackets were not used for the calculation of the mean values.

Table 3-12: IDA-72: Calculated Laboratory Mean Values of the Isotopic Composition of Sample B(unspiked)

Relative Isopic Abundances [atom %]

Lab. Code	U-233	U-234	U-235	U-236	U-238
2	0.00012	0.0165	2.155	0.3821	97.446
3	-	0.0170	2.140	0.3854	97.458
4	-	-	2.177	0.4011	97.422
5	-	0.0194	2.174	0.3816	97.425
6	-	0.0160	2.180	0.3850	97.419
7	-	0.0149	2.152	0.3801	97.453
8	0.00727	0.0180	2.181	0.3730	97.421
10	0.00022	0.0161	2.148	0.3796	97.456
12	-	-	2.171	0.3858	97.443
13	-	0.0194	2.163	0.3798	97.438
14	-	0.0159	2.160	0.3861	97.439
15	-	0.0174	2.175	0.3858	97.422
16	-	0.0162	2.185	0.3873	97.412
17	-	0.0158	2.157	0.3831	97.444
18	-	0.0175	2.186	0.3803	97.416
19	-	0.0167	2.146	0.3807	97.457
20	-	0.0135	2.135	0.3712	97.481
21	-	-	2.170	0.3841	97.446
23	-	-	(2.203)	-	(97.797)
Mean of means:		0.0167	2.164	0.3829	97.439
SD		0.0015	0.016	0.0063	0.019
RSD [%]		9.26	0.73	1.64	0.02

Values in brackets were not used for the calculation of the mean values.

Table 3-13: IDA-72: Calculated Laboratory Mean Values of the Isotopic Composition of Sample R(unspiked)

Lab. Code	U-233	U-234	U-235	U-236	U-238
	Relative Isotopic Abundances [atom %]				
2	0.00005	0.0059	0.7214	0.00075	99.272
3	0.00374	0.0066	0.7204	-	99.269
4	-	-	0.7207	-	99.279
5	-	0.0099	0.7326	-	99.257
6	-	0.0066	0.7274	-	99.266
7	-	0.0035	0.7099	-	99.287
8	0.00947	0.0056	0.7263	-	99.259
10	0.00023	0.0052	0.7165	0.00013	99.278
12	-	0.0055	0.7179	-	99.277
13	-	-	0.7211	-	99.279
14	-	0.0050	0.7215	-	99.273
15	-	0.0068	0.7306	-	99.263
16	-	-	0.7208	-	99.279
17	-	0.0051	0.7184	-	99.276
18	-	0.0039	0.7267	-	99.269
19	-	0.0059	0.7135	-	99.281
20	-	0.0048	0.7086	-	99.287
21	-	-	(2.824)	(0.1906)	(96.985)
23	-	-	0.7144	-	99.286
Mean of means :		0.0057	0.7205	-	99.274
SD		0.0015	0.0066		0.009
RSD [%]		26.7	0.91	-	0.01
CBNM		0.0055	0.7203	-	99.2742

Values in brackets were not used for the calculation of the mean values.

3.4.2 Plutonium

The calculated isotopic compositions of the unspiked samples A, B and R are compiled in Tables 3-14 to 3-16. At the foot of the tables, the calculated means of the laboratory means, the standard deviations and the relative standard deviations of the laboratory mean values are given.

The data omitted from these calculations as outliers or because of uncompleteness are marked in the tables accordingly.

Calculation of the Pu-238 abundance was always based on the α-spectrometric determination. If only mass spectrometric data were available, these were used. In cases, where neither mass spectrometric measurements nor α-spectrometric measurements were given, for samples A and B the isotopic composition was calculated as if no Pu-238 was found. For the calculation of the means of laboratory means the data of these laboratories were not used, because they are biased by this method. In the case of the R-sample the Pu-238 content is so low that the influence of this bias can be neglected.

The calculated mean values for the isotopic composition of the unspiked samples A and B are in good agreement. The rather high value of the standard deviation for Pu-238 (sample A) is caused by the measurement of laboratory 16. Exclusion of this value reduces the relative standard deviation to about 1 %.

At the foot of Tab. 3-16 the calculated mean values of the unspiked R-sample are compared with the data stated by CBNM for its composition. Satisfactory agreement exists for the abundant isotopes, for the rare ones, however, agreement is rather poor.

Table 3-14: IDA-72 : Calculated Laboratory Mean Values of the Isotopic Composition of Sample A (unspiked)

Relative Isotopic Abundances [atom %]

Lab. Code	Method used for Pu-238 determination	Pu-238	Pu-239	Pu-240	Pu-241	Pu-242	Reason for rejection
2	none	-	(72.106)	(16.628)	(9.576)	(1.691)	no Pu-238 measurement
3	α	1.048	71.491	16.571	9.235	1.655	
4	α	1.028	71.634	16.510	9.200	1.627	
5	α	1.045	71.795	16.551	8.983	1.627	
6	α	1.057	71.605	16.538	9.147	1.653	
7	α	1.042	71.661	16.535	9.110	1.652	
8	MS	(1.085)	(71.330)	(16.385)	(9.215)	(1.985)	Pu-242/Pu-239 outlier
10	MS	1.046	71.709	16.479	9.125	1.640	
12	none	-	(72.402	(16.697)	(9.244)	(1.657)	no Pu-238 measurement
13	α	1.054	71.704	16.526	9.095	1.621	
14	MS	1.074	71.728	16.507	9.055	1.636	
15	α	1.053	71.620	16.539	9.137	1.651	
16	MS	1.159	71.452	16.582	9.162	1.646	
17	α	1.053	71.661	16.536	9.113	1.637	
18	α	1.048	71.648	16.514	9.144	1.646	
19	α	1.058	71.748	16.515	9.062	1.618	
20	none	-	(72.373)	(16.769)	(9.216)	(1.642)	no Pu-238 measurement
21	α	(0.655)	(71.930)	(16.605)	(9.072)	(1.738)	Pu-238/Pu-239 outlier
Mean of means		1.059	71.650	16.531	9.121	1.639	
SD		0.032	0.096	0.027	0.065	0.013	
RSD [%]		3.01	0.13	0.17	0.71	0.77	

Values in brackets were not used for the calculation of mean value, SD and RSD

Table 3-15: IDA-72 : Calculated Laboratory Mean Values of the Isotopic Composition of Sample B(unspiked)

Lab. Code	Method used for Pu-238 determination	Relative Isotopic Abundances [atom %] Pu-238	Pu-239	Pu-240	Pu-241	Pu-242	Reason for rejection
2	none	-	(72.219)	(16.655)	(9.443)	(1.683)	no Pu-238 measurement
3	α	1.047	71.621	16.514	9.148	1.669	
4	α	1.035	71.763	16.457	9.131	1.613	
5	α	(0.862)	(71.840)	(16.579)	(9.094)	(1.625)	Pu-238/Pu-239 outlier
6	α	1.047	71.619	16.544	9.140	1.651	
7	α	1.043	71.704	16.487	9.126	1.641	
8	MS	1.073	71.842	16.341	9.039	1.705	
10	MS	1.047	71.762	16.452	9.098	1.641	
12	none	-	(72.400)	(16.696)	(9.236)	(1.667)	no Pu-238 measurement
13	α	1.045	71.724	16.496	9.101	1.634	
14	MS	1.070	71.620	16.540	9.122	1.648	
15	α	1.060	71.660	16.517	9.116	1.647	
16	MS	1.054	71.611	16.584	9.115	1.637	
17	α	1.049	71.641	16.525	9.145	1.640	
18	α	1.021	71.714	16.513	9.104	1.648	
19	α	1.055	71.762	16.495	9.070	1.618	
20	none	-	(72.623)	(16.666)	(9.163)	(1.548)	no Pu-238 measurement
21	α	(0.716)	(71.929)	(16.589)	(9.081)	(1.685)	Pu-238/Pu-239 outlier
Mean of means		1.050	71.696	16.497	9.112	1.646	
SD		0.014	0.073	0.059	0.031	0.023	
RSD [%]		1.30	0.10	0.36	0.34	1.38	

Values in brackets were not used for the calculation of mean value, SD and RSD

Table 3-16: IDA-72 : Calculated Laboratory Mean Values of the Isotopic Composition of Sample R(unspiked)

Relative Isotopic Abundances [atom %]

Lab. Code	Method used for Pu-238 determination	Pu-238	Pu-239	Pu-240	Pu-241	Pu-242	Reason for rejection
2	none	-	97.345	2.569	0.0803	0.00536	
3	α	0.00387	97.338	2.584	0.0712	0.00303	
4	α	(0.00383)	(97.708)	(2.288)	-	-	no Pu-241measurement, Pu-240/Pu-239 outlier
5	α	0.00358	97.222	2.692	0.0820	-	
6	α	0.00663	97.326	2.581	0.0770	0.00973	
7	α	0.00371	97.394	2.522	0.0778	0.00235	
8	MS	(0.02916)	(97.188)	(2.657)	(0.0964)	(0.02916)	Pu-241/Pu-239 outlier
10	MS	0.00697	97.340	2.577	0.0724	0.00314	
12	none	-	97.363	2.565	0.0724	-	
13	α	0.00755	97.376	2.547	0.0695	-	
14	MS	0.00933	97.334	2.580	0.0739	0.00284	
15	α	0.00389	97.351	2.564	0.0761	0.00482	
16	none	-	97.375	2.550	0.0718	0.00336	
17	α	0.00378	97.367	2.556	0.0705	0.00296	
18	α	0.00362	97.366	2.554	0.0725	0.00449	
19	none	-	97.361	2.561	0.0728	0.00494	
20	none	-	97.392	2.541	0.0662	-	
21	α	(0.02597)	(97.128)	(2.717)	(0.1295)	-	Pu-238/Pu-239 and Pu-241/Pu-239outlier
Mean of means		0.00529	97.350	2.570	0.0738	0.00427	
	SD	0.00212	0.041	0.038	0.0042	0.00207	
	RSD	40.1	0.04	1.47	5.68	48.4	
CBNM		0.0039	97.355	2.565	0.0724	0.0032	

Values in brackets were not used for the calculation of mean value, SD and RSD

3.5 Calculated Concentrations

3.5.1 Method of Calculation

Because of the outlier values in the isotopic ratio determinations /Par. 3.2.1 and Par. 3.2.2/ and the uncomplete Pu-238 data /Par. 3.3.1/ it seemed advisable to compare the concentrations obtained by the individual laboratories in such a way that they are independent on the completeness of the isotopic composition measurements. Therefore, the concentrations were calculated in terms of atoms/g solution for the main isotopes U-238 and Pu-239, respectively, and not, as usual, in terms of g element/g solution.

This concentration is given by

$$C = \frac{(1-RR_s)}{R-R_u} \cdot \frac{G_s}{G_u} \cdot S$$

with

R = Ratio U-233/U-238 or Pu-242/Pu-239 of the spiked sample

R_u = Ratio U-233/U-238 or Pu-242/Pu-239 of the unspiked sample

R_s = Ratio U-238/U-233 or Pu-239/Pu-242 of the mixed spike solution

G_s and G_u = Masses of the aliquots of mixed spike and unspiked solution

S = Number of atoms U-233 or Pu-242 per gram of the mixed spike solution.

According to the layout of this experiment, three individual chemical preparations of the spiked samples with following mass spectrometric determination of the isotopic ratios U-233/U-238 and Pu-242/Pu-239 were performed /Fig. 3-1/.

Using for R in the formula the three run mean values obtained by this procedure, and for R_u and R_s always the laboratory mean values, three concentration values could be calculated for each sample and laboratory. From these values finally the laboratory means and their relative standard deviations were calculated. The numerical values of the laboratory mean values for R, R_u and in the case of uranium also for R_s are given in Vol. II, Par. 12.3. In the case of plutonium, the value 0.0134 calculated from the isotopic composition determination of the mixed spike solution by CBNM /Tab. 2-1/ was used for R_s for all laboratories, because the individual laboratories measured for this isotopic ratio the slightly different value of the Pu-242 single spike solution /Par. 3.1/.

The concentration S of the U-233 and Pu-242 isotopes in the mixed spike solution were calculated to be

$2.0931 \cdot 10^{18}$ atoms U-233/g mixed spike solution

and $2.4594 \cdot 10^{16}$ atoms Pu-242/g mixed spike solution

from the data reported by CBNM / Tab. 2-1 and Vol. II, Par. 3.2.2/.

The aliquots G_s and G_u of the spiking procedure stated by CBNM /Vol. II, Par. 3.2.2 to Par. 3.2.5/ are compiled in Table 3-17.

Table 3-17: IDA-72: Aliquotation of Sample Solutions

Sample	Aliquot of mixed spike solution G_s [g]	Aliquot of unspiked sample solution G_u [g]
A	47.114	52.154
B	47.157	55.377
R	46.628	45.943

Besides the concentration values obtained as explained before, so-called "calibrated" values C^* were calculated for the samples A and B according to

$$C_i^*(A,B) = C_i(A,B)\ \frac{C_o(R)}{C_i(R)}$$

with

$C_i(A,B)$ = Mean value obtained by laboratory i for the concentration of sample A or B (calculated using the formula given before).

$C_o(R)$ = Theoretical concentration of R-sample as stated by CBNM /Tab.2-1/.

$C_i(R)$ = Mean value obtained by laboratory i for the concentration of sample R.

By this way of "calibration" against the reference solution R error contributions due to insufficient mass discrimination corrections can be cancelled. This is meaningful, as such errors are compensated in practice if the spike solution is calibrated by the same individual laboratory which performs the analysis /Vol. II, Par. 7.1/.

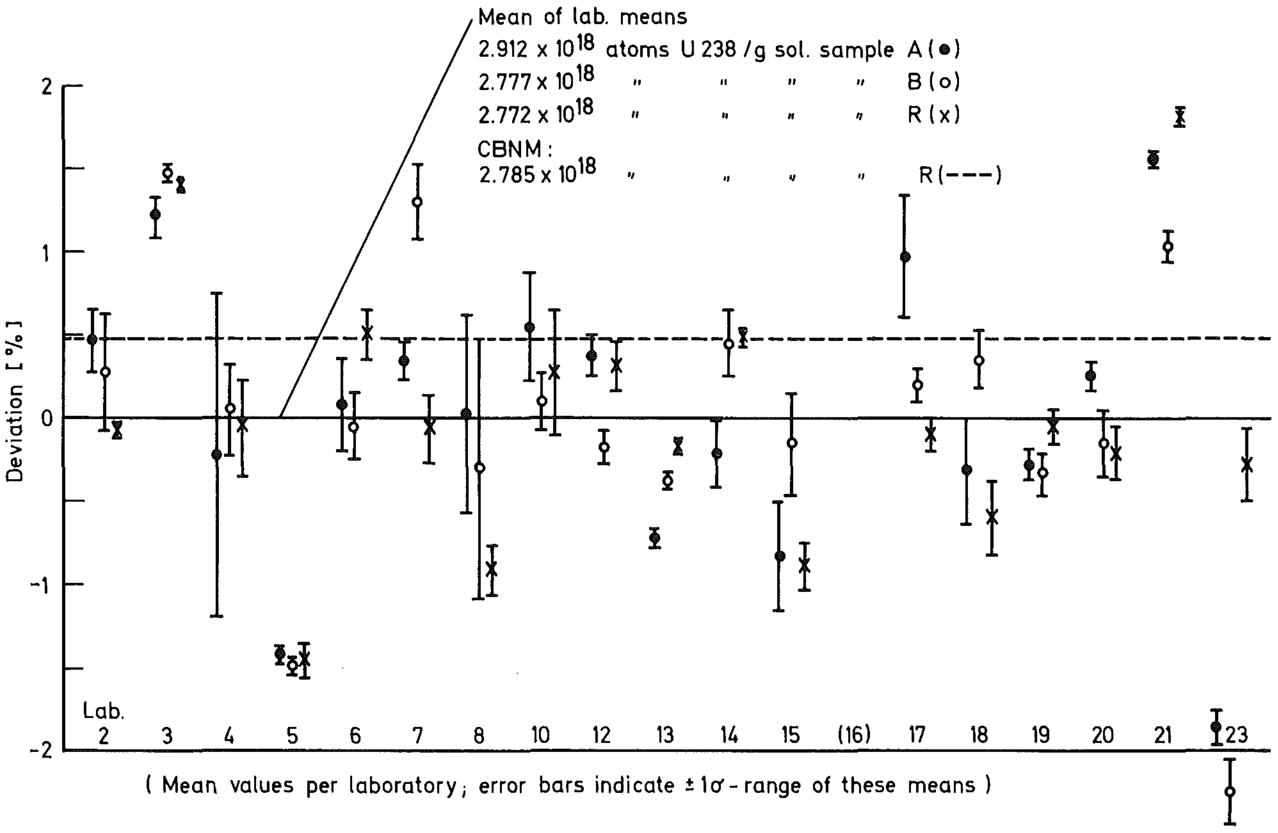
3.5.2 Uranium

The calculated U-238 concentrations are compiled in Tab. 3-18. The "calibrated" values given in columns 8 and 12 were obtained using for $C_i(R)$ the laboratory means of the R-sample shown in column 3 and for $C_o(R)$ the value 2.785×10^{18} atoms/g sol. stated by CBNM /Tab.2-1/. A graphic presentation of these results is given in Fig. 3-35 and 3-37.

Table 3-18: IDA-72: U-238 Concentrations Calculated for Samples R, A and B

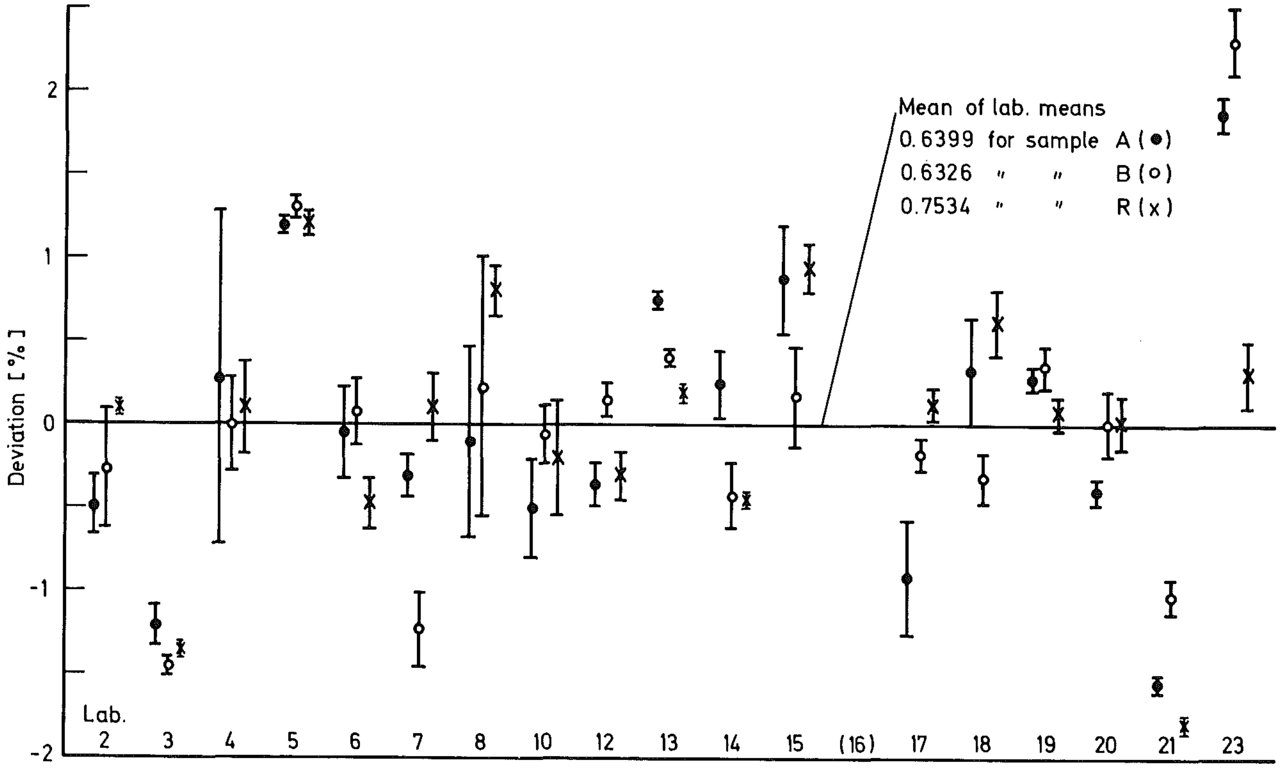
Column	1	2	3	4	5	6	7	8	9	10	11	12
		Sample R			Sample A				Sample B			
Lab.Code	Number of MS-run	U-238 concentration per run [x 10^{18} $\frac{\text{atoms}}{\text{g sol.}}$]	Lab.mean U-238 concentration [x 10^{18} $\frac{\text{atoms}}{\text{g sol.}}$]	RSD of lab. mean [%]	U-238 concentration per run [x 10^{18} $\frac{\text{atoms}}{\text{g sol.}}$]	Lab.mean U-238 concentration [x 10^{18} $\frac{\text{atoms}}{\text{g sol.}}$]	RSD of lab. mean [%]	Lab.mean U-238 concentration "calibrated" with sample R[1] [x 10^{18} $\frac{\text{atoms}}{\text{g sol.}}$]	U-238 concentration per run [x 10^{18} $\frac{\text{atoms}}{\text{g sol.}}$]	Lab.mean U-238 concentration [x 10^{18} $\frac{\text{atoms}}{\text{g sol.}}$]	RSD of lab. mean [%]	Lab.mean U-238 concentration "calibrated" with sample R[1] [x 10^{18} $\frac{\text{atoms}}{\text{g sol.}}$]
2	1	2.770	2.770	.02	2.931	2.927	.18	2.944	2.798	2.785	.36	2.802
	2	2.769			2.933				2.765			
	3	2.770			2.916				2.793			
3	1	2.809	2.811	.02	2.942	2.948	.13	2.922	2.817	2.818	.05	2.794
	2	2.812			2.955				2.322			
	3	2.811			2.948				2.817			
4	1	2.760	2.770	.29	2.948	2.906	.97	2.922	2.767	2.779	.28	2.795
	2	2.786			2.919				2.794			
	3	2.764			2.852				2.775			
5	1	2.727	2.732	.09	2.871	2.871	.01	2.928	2.734	2.736	.05	2.790
	2	2.732			2.871				2.738			
	3	2.736			2.871				2.735			
6	1	2.777	2.786	.16	2.915	2.915	.28	2.915	2.768	2.776	.20	2.776
	2	2.793			2.929				2.774			
	3	2.787			2.901				2.786			
7	1	2.775	2.770	.21	2.919	2.922	.13	2.939	2.815	2.813	.23	2.830
	2	2.776			2.930				2.824			
	3	2.759			2.918				2.802			
8	1	2.755	2.747	.14	2.894	2.913	.59	2.955	2.790	2.769	.77	2.809
	2	2.742			2.948				2.727			
	3	2.744			2.900				2.792			
10	1	2.775	2.779	.37	2.932	2.928	.32	2.935	2.777	2.781	.17	2.787
	2	2.799			2.911				2.774			
	3	2.765			2.943				2.790			
12	1	2.773	2.781	.15	2.919	2.923	.13	2.929	2.779	2.774	.11	2.779
	2	2.786			2.931				2.768			
	3	2.784			2.920				2.774			
13	1	2.768	2.767	.04	2.892	2.892	.03	2 .911	2.765	2.767	.03	2.786
	2	2.769			2.890				2.769			
	3	2.765			2.893				2.767			
14	1	2.787	2.785	.04	2.894	2.906	.20	2.907	2.779	2.790	.21	2.791
	2	2.783			2.911				2.798			
	3	2.786			2.913				2.794			
15	1	2.755	2.747	.15	2.875	2.888	.32	2.929	2.761	2.774	.30	2.813
	2	2.740			2.906				2.789			
	3	2.746			2.883				2.770			
17	1	2.774	2.769	.10	2.962	2.941	.37	2.959	2.786	2.783	.11	2.800
	2	2.764			2.930				2.786			
	3	2.767			2.930				2.777			
18	1	2.767	2.755	.22	2.922	2.903	.32	2.936	2.796	2.787	.17	2.818
	2	2.748			2.894				2.787			
	3	2.751			2.894				2.780			
19	1	2.776	2.770	.10	2.904	2.905	.08	2.922	2.762	2.768	.13	2.784
	2	2.768			2.902				2.768			
	3	2.767			2.909				2.775			
20	1	2.770	2.766	.15	2.916	2.920	.08	2.941	2.781	2.773	.21	2.793
	2	2.758			2.921				2.776			
	3	2.771			2.923				2.762			
21	1	2.821	2.822	.03	2.958	2.958	.04	2.920	2.807	2.806	.10	2.770
	2	2.823			2.959				2.801			
	3	2.822			2.955				2.810			
23	1	2.775	2.764	.23	2.861	2.859	.10	2.882	2.705	2.715	.20	2.737
	2	2.764			2.853				2.716			
	3	2.753			2.863				2.724			
Means of means			2.772			2.913		2.928		2.777		2.792
SD			0.021			0.025		0.019		0.024		0.020
RSD [%]			0.76			0.86		0.64		0.87		0.73

[1] For explanation see Par. 3.5.1.



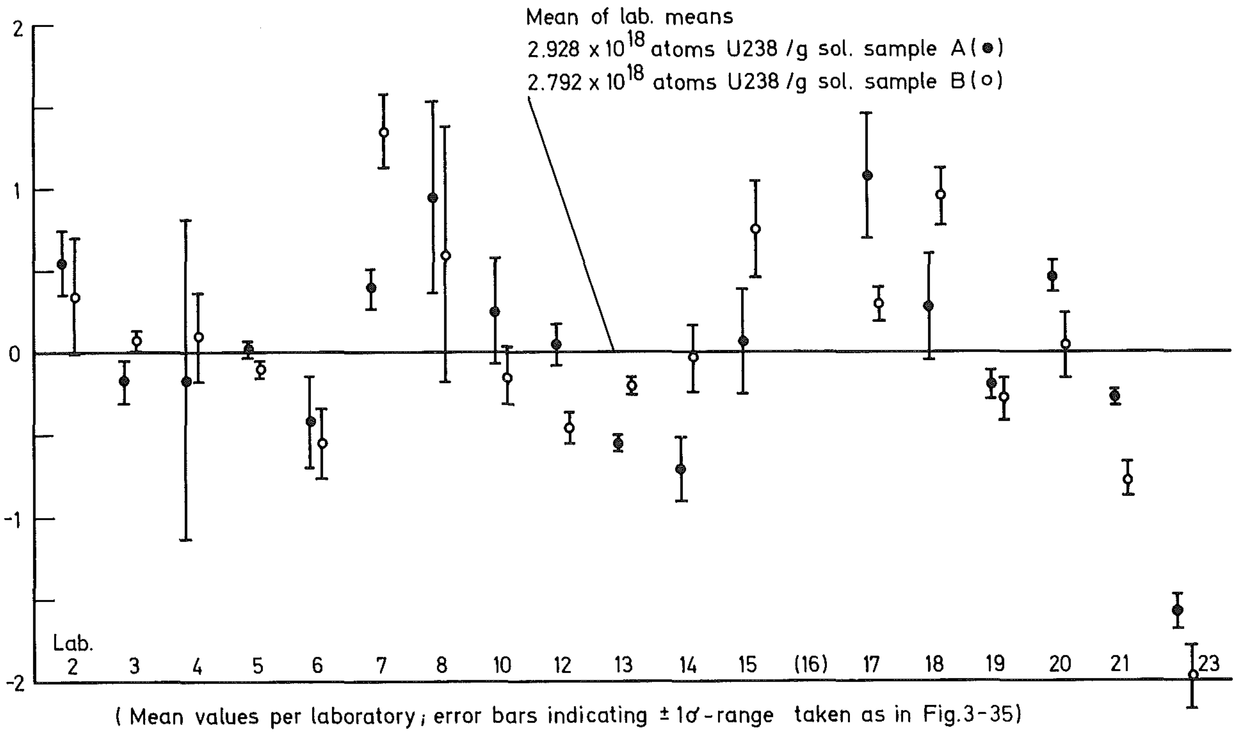
(Mean values per laboratory; error bars indicate ± 1σ - range of these means)

Fig. 3-35 IDA-72 : U238 Concentration of Samples A, B and R



(Mean values per laboratory; error bars indicate ± 1σ - range of these means)

Fig. 3-36 IDA-72 : MS - Determinations of Isotopic Ratio U233 / U238 of Spiked Samples A, B and R



(Mean values per laboratory; error bars indicating ± 1σ-range taken as in Fig.3-35)

Fig. 3-37IDA-72 : U238 Concentration of Samples A and B after "Calibration" with Sample R

As R_s and R_u in the concentration formula /Par. 3.5.1/ are small compared to R, in this experiment errors in the concentration values are nearly exclusively determined by the error of the isotopic ratio U-233/U-238, measured on the spiked samples. This is clearly demonstrated in Fig. 3-36 (which is identical with Fig. 3-3 of Par. 3.2.1) showing these isotopic ratios in the usual manner. It is nearly the "mirror image" of Fig. 3-35.

The dashed line in Fig. 3-35 indicates the U-concentration of the synthetic reference solution of CBNM / Tab.2-1 / for which an accuracy of better than ± 0.1 % is stated /Vol. II,Par.3.2.1/.This value is 0.48 % higher than the calculated mean of the laboratory means of the R-sample. Besides the uncertainty of less than 0.1 % for the theoretical concentration of the R-solution, errors in the spike solution concentration, stated by CBNM with less than ± 0.25 %, eventual aliquotation errors and the uncertainty of the mean value of the means, calculated for the analytical determined concentration values, contribute to this difference. For this mean of the means a relative standard deviation of about ± 0.18 can be calculated on the basis of the laboratory mean values /Tab. 3-18/.

3.5.3 Plutonium

The calculated Pu-239 concentrations are compiled in Tab. 3-19. The "calibrated" values given in columns 8 and 12 were obtained using for $C_i(R)$ the laboratory means of the R-sample shown in column 3 and for $C_o(R)$ the value 2.109×10^{16} atoms/g sol. stated by CBNM / Tab.2-1 /. A graphic presentation of these results is given in Fig. 3-38 and 3-40.

As opposed to the results obtained for uranium, there is a number of values which deviates so much from the majority that these values had to be considered as outliers and were not used to calculate the means of the laboratory means. Two explanations were given for these effects by the analysts participating in the final working group sessions of this experiment / Par.8.3.1 and 8.5 /:
cross contamination with material of other isotopic composition or, in some cases more likely, insufficient valency adjustment between the spike plutonium and the sample plutonium, causing a non-uniform behaviour of these two chemically different plutonium components in the following steps for the uranium separation / Vol.II,Chapt.6/ 1).

It should be noted that in some cases the satisfactory reproducibility of the repetition measurements assured the laboratories to consider their results as correct. They could only be identified as outliers by comparison with the data obtained by other laboratories.

As an example, attention is drawn to the case of laboratory 6. The result on sample A is very close to the mean of laboratory means, those on sample B and R, however, deviate by more than 10 %. As the relative standard deviations of the laboratory mean value for the B-sample was only 0.34 %, there was no reason at all for the laboratory to distrust this result. On special request, this experienced laboratory confirmed that the spiked samples passed the chemical preparation step for each run separately in accordance with the experimental layout described in Par. 3.1 and that throw-away parts were used without exception.

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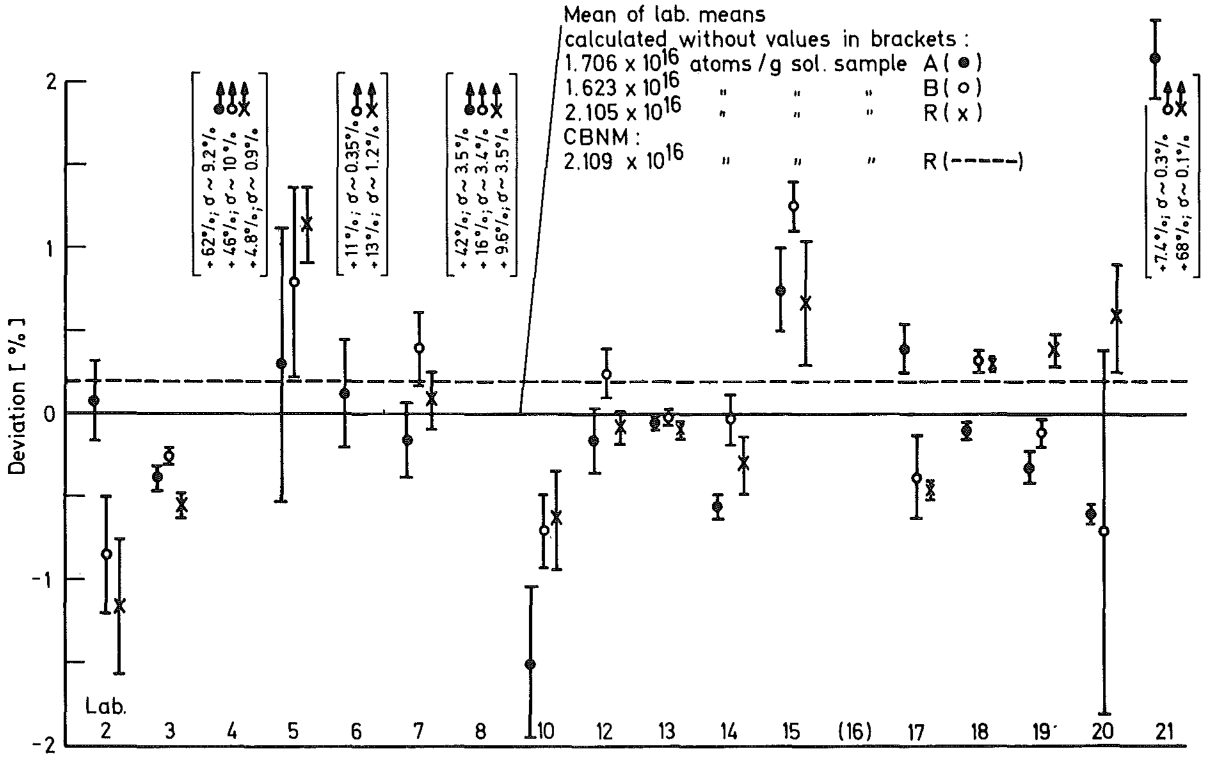
1) In this experiment, valency adjustment was complicated by the fact that plutonium-VI was used for the spike.

Table 3-19: IDA-72: Pu-239 Concentration Calculated for Samples R,A and B

Column 1		2	3	4	5	6	7	8	9	10	11	12
		Sample R			Sample A				Sample B			
Lab.Code	Number of MS-run	Pu-239 concentration per run [x 10^{16} $\frac{\text{atoms}}{\text{g sol.}}$]	Lab.mean Pu-239 concentration [x 10^{16} $\frac{\text{atoms}}{\text{g sol.}}$]	RSD of lab. mean [%]	Pu-239 concentration per run [x 10^{16} $\frac{\text{atoms}}{\text{g sol.}}$]	Lab.mean Pu-239 concentration [x 10^{16} $\frac{\text{atoms}}{\text{g sol.}}$]	RSD of lab. mean [%]	Lab.mean Pu-239 concentration "calibrated" with sample R[1] [x 10^{16} $\frac{\text{atoms}}{\text{g sol.}}$]	Pu-239 concentration per run [x 10^{16} $\frac{\text{atoms}}{\text{g sol.}}$]	Lab.mean Pu-239 concentration [x 10^{16} $\frac{\text{atoms}}{\text{g sol.}}$]	RSD of lab. mean [%]	Lab.mean Pu-239 concentration "calibrated" with sample R[1] [x 10^{16} $\frac{\text{atoms}}{\text{g sol.}}$]
2	1	2.084	2.081	.40	1.716	1.708	.24	1.732	1.602	1.610	.34	1.632
	2	2.093			1.703				1.620			
	3	2.065			1.704				1.607			
3	1	2.091	2.094	.07	1.698	1.700	.07	1.713	1.621	1.619	.06	1.631
	2	2.095			1.702				1.618			
	3	2.095			1.700				1.618			
4	1	2.227	(2.206)	.89	2.787	(2.765)	9.17	(2.644)	2.064	(2.364)	10.01	(2.261)
	2	2.225			2.377				2.290			
	3	2.167			3.270				2.874			
5	1	2.124	2.129	.22	1.733	1.711	.82	1.696	1.631	1.636	.57	1.622
	2	2.125			1.716				1.624			
	3	2.138			1.685				1.654			
6	1	2.438	(2.382)	1.15	1.719	1.708	.33	(1.513)	1.795	(1.803)	.35	(1.597)
	2	2.359			1.706				1.799			
	3	2.352			1.700				1.816			
7	1	2.104	2.107	.17	1.706	1.704	.22	1.706	1.636	1.629	.22	1.632
	2	2.114			1.709				1.628			
	3	2.103			1.696				1.624			
8	1	2.466	(2.307)	3.50	2.486	(2.419)	3.54	(2.212)	1.879	(1.879)	3.42	(1.718)
	2	2.281			2.256				1.774			
	3	2.191			2.535				1.997			
10	1	2.084	2.092	.29	1.673	1.681	.44	1.695	1.619	1.612	.22	1.626
	2	2.104			1.696				1.608			
	3	2.088			1.673				1.608			
12	1	2.099	2.104	.11	1.697	1.704	.19	1.709	1.632	1.627	.16	1.632
	2	2.104			1.706				1.623			
	3	2.107			1.708				1.626			
13	1	2.104	2.103	.04	1.706	1.706	.01	1.711	1.622	1.623	.03	1.628
	2	2.101			1.706				1.623			
	3	2.104			1.705				1.623			
14	1	2.106	2.099	.17	1.696	1.697	.08	1.706	1.623	1.623	.16	1.631
	2	2.093			1.695				1.618			
	3	2.098			1.699				1.627			
15	1	2.125	2.119	.38	1.714	1.719	.24	1.711	1.649	1.644	.15	1.637
	2	2.104			1.716				1.642			
	3	2.129			1.727				1.641			
17	1	2.097	2.096	.05	1.710	1.713	.14	1.725	1.620	1.617	.25	1.628
	2	2.093			1.717				1.609			
	3	2.097			1.712				1.622			
18	1	2.112	2.111	.02	1.705	1.705	.04	1.704	1.630	1.628	.07	1.627
	2	2.111			1.703				1.626			
	3	2.111			1.705				1.629			
19	1	2.109	2.113	.09	1.698	1.701	0.10	1.698	1.624	1.621	.08	1.619
	2	2.115			1.704				1.620			
	3	2.115			1.700				1.620			
20	1	2.131	2.118	.32	1.695	1.696	.06	1.690	1.599	1.612	1.11	1.606
	2	2.112			1.695				1.648			
	3	2.110			1.698				1.590			
21	1	3.527	(3.530)	.01	1.750	1.743	.23	(1.042)	1.745	(1.743)	.33	(1.042)
	2	3.534			1.737				1.752			
	3	--			1.742				1.732			
Means of means			2.105			1.706		1.707		1.623		1.627
SD			0.013			0.013		0.012		0.010		0.008
RSD [%]			0.62			0.78		0.69		0.60		0.48

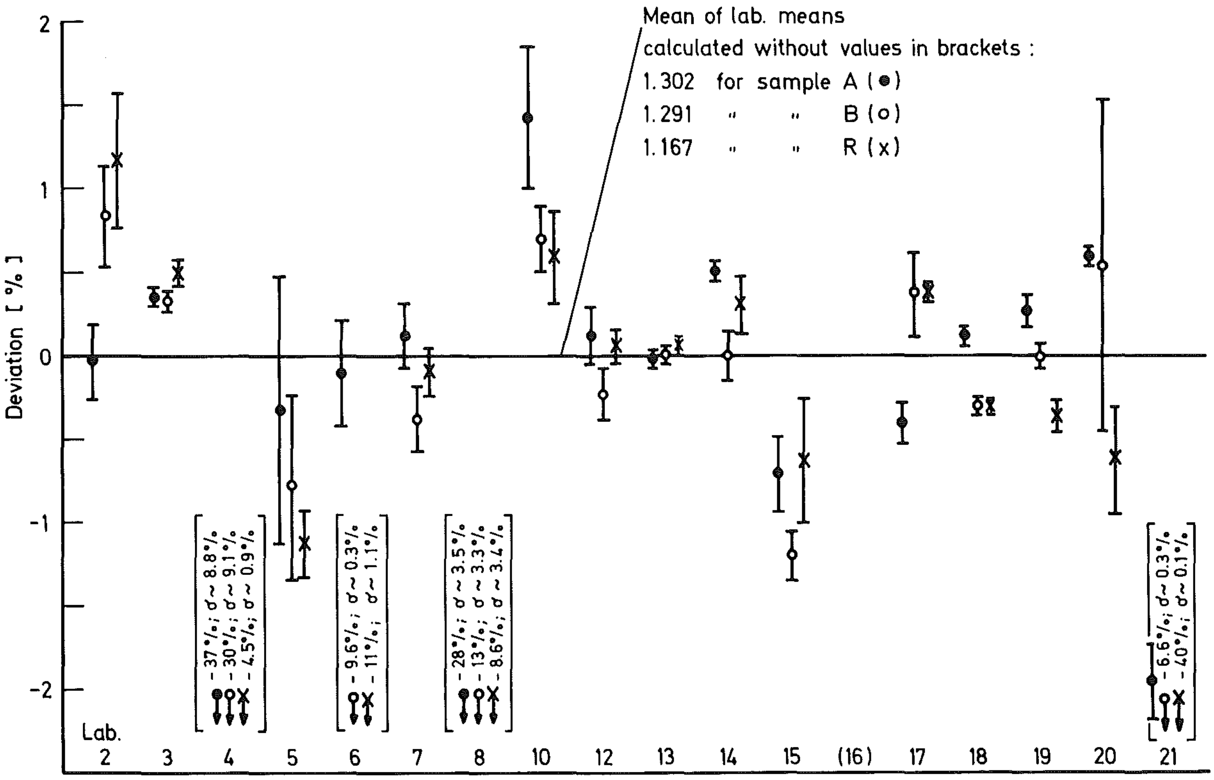
Values in brackets were not used for the calculation of mean value, SD and RSD.

[1] For explanation see Par. 3.5.1.



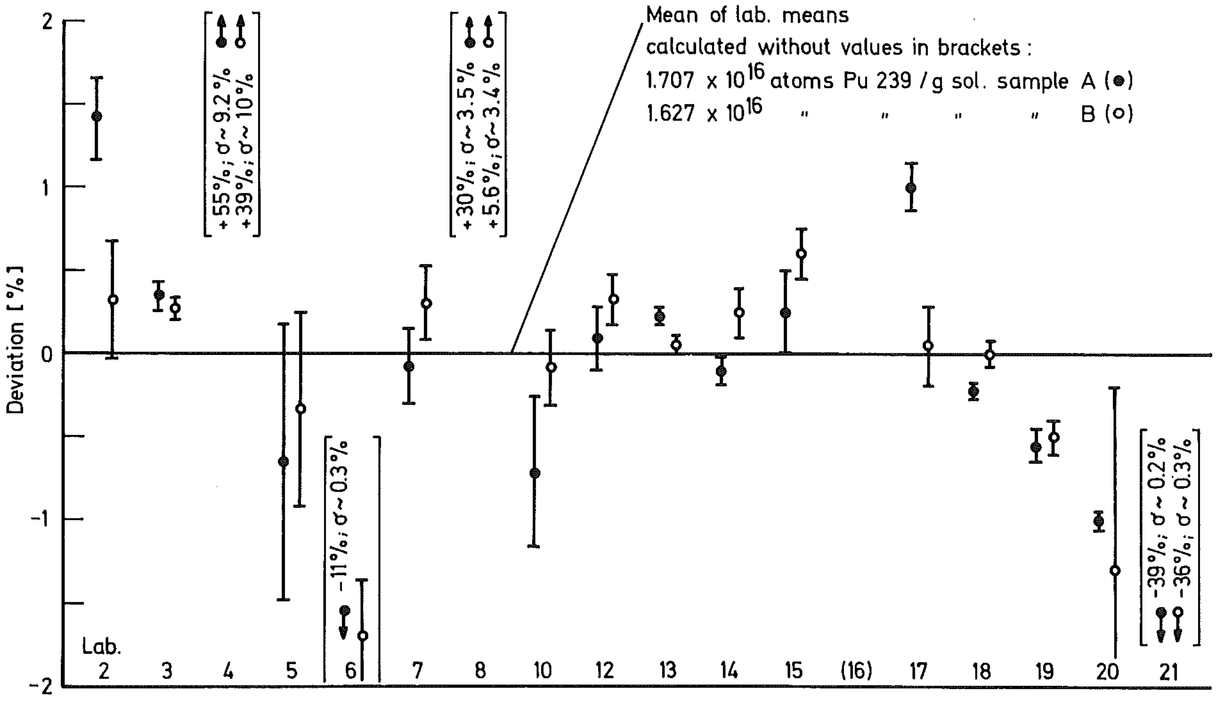
(Mean values per laboratory ; error bars indicate ± 1σ - range of these means)

Fig. 3-38 IDA-72 : Pu 239 Concentration of Samples A, B and R



(Mean values per laboratory ; error bars indicate ± 1σ - range of these means)

Fig. 3-39 IDA-72 : MS - Determinations of Isotopic Ratio Pu 242 / Pu 239 of Spiked Samples A, B and R



(Mean values per laboratory; error bars indicating ± 1σ - range taken as in Fig. 3-38)

Fig.3-40 IDA-72: Pu 239 Concentration of Sample A and B after "Calibration" with Sample R

The dashed line in Fig. 3-38 indicates the Pu-concentration of the synthetic reference solution as given by CBNM / Tab. 2-1 / with an accuracy of better than ± 0.1 % /Vol. II, Par.3.2.1/.Its value is 0.19% higher than the calculated mean of the laboratory means of the R-sample. Concerning the errors which may contribute to this difference, the same considerations as in the case of uranium are valid /Par. 3.5.2/. For the relative standard deviation of the mean of the means ± 0.17 % is calculated /Tab. 3-19/.

Again, as in the case of uranium, errors in the isotopic ratio determinations of the spike and unspiked sample have no significant influence on the error of the Pu-239 concentration values, which are nearly exclusively determined by the error of the isotopic ratio Pu-242/Pu-239, measured on the spiked sample. For demonstration, these isotopic ratios are shown in Fig. 3-39 which is identical with Fig. 3-27, shown in Par. 3.2.2.

3.5.4 Calculation of Estimates for Relative Standard Deviations of Error Components

By analysis of variances - based on the three concentration values obtained for each laboratory and sample from the three run means of the U-233/U-238 and Pu 242/Pu-239 ratio, respectively /Tab. 3-18 and 3-19/ - estimates were calculated for the precision and the interlaboratory deviation of the concentration determinations. According to the experimental layout /Par. 3.1/ the precision describes the deviation obtained by repeated analyses of the same sample within one individual laboratory and includes all randomly distributed errors of chemical sample preparation and/or mass spectrometric measurements /Par. 2.5/. The interlaboratory deviation is caused in this experiment only by specific laboratory errors - if sample contamination before its distribution to the laboratories is not taken into consideration - as due to the common spiking of the sample solution for all laboratories neither the spiking itself nor any changes in sample composition (e.g. by evaporation) contribute to this error component. The results are given in columns 1 and 2 of Table 3-20.

Table 3-20: IDA-72: Calculated RSD of Error Components for the U-238 and Pu-239 Concentration Determinations.

Column	1		2		3	
Sample	Precision RSD [%]		Interlab. deviation RSD [%]		Interlab. deviation after "calibration" with R-sample RSD [%]	
	U	Pu	U	Pu	U	Pu
R	0.29	0.38	0.75	0.59	-	-
A	0.57	0.51¹⁾	0.79	0.59¹⁾	0.52	0.62 (0.78)²⁾
B	0.46	0.66¹⁾	0.84	0.48¹⁾	0.68	0.30 (0.53)²⁾

---

1) Calculated for the same group of laboratories as in the case of "calibrated" values (column 3).

2) The values in brackets are calculated on the basis of Pu-element concentrations.

The estimates of the precision are smaller for the R-solution than for the A and B sample. This may reflect the better conditions for analysing clean sample material than solutions contaminated with fission products.

The reduction of the interlaboratory deviation value by using "calibrated" data (column 3) is more pronounced for uranium than for plutonium. This may indicate that the method of mass discrimination correction - being more important for uranium than for plutonium - mainly contributes to this error component. However, it has to be kept in mind that for plutonium the calculation was made after the rejection of several outliers.

For uranium no significant changes in the results of the error considerations have to be expected if they are based on U-element concentrations instead of U-238 concentrations because of the nearly monoisotopic sample material / Tab. 2-1 /. In the case of plutonium, however, the composition in sample A and B cannot be considered as monoisotopic / Tab. 2-1 /. Therefore, in order to estimate the changes in the results of the error considerations which have to be expected if they are based on plutonium element concentrations instead of Pu-239 concentrations, the interlaboratory deviations were also calculated for that case. They amount to 0.78 and 0.53 % for samples A and B, respectively, as given in brackets in column 3 of Table 3-20.

3.5.5 Concentration Ratio Pu-239/U-238

For verification whether or not Pu/U concentration ratios show less interlaboratory deviation than the concentrations separately, the Pu-239/U-238 ratios, based on the laboratory mean values, were calculated. They are compiled in Table 3-21 together with the concentration values for U-238 and Pu-239 separately, in order to facilitate comparison of the relative standard deviations of the laboratory mean values, given at the foot of the table. As it can be seen, there is no indication that smaller limits of error can be expected if Pu/U-concentration ratios are considered instead of the concentrations of the individual elements.

Table 3-21: IDA-72: Pu-239/U-238 Concentration Ratios Calculated for Samples A, B and R.

Lab. Code	Sample A			Sample B			Sample R		
	Concentration		Atomic ratio	Concentration		Atomic ratio	Concentration		Atomic ratio
	U-238 $\left[x10^{18}\ \frac{atoms}{g\ sol.}\right]$	Pu-239 $\left[x10^{16}\ \frac{atoms}{g.sol}\right]$	$\frac{Pu-239}{U-238}$ $\left[x\ 10^{-2}\right]$	U-238 $\left[x10^{18}\ \frac{atoms}{g\ sol}\right]$	Pu-239 $\left[x10^{16}\ \frac{atoms}{g\ sol}\right]$	$\frac{Pu-239}{U-238}$ $\left[x\ 10^{-2}\right]$	U -238 $\left[x10^{18}\ \frac{atoms}{g\ sol.}\right]$	Pu-239 $\left[x10^{16}\ \frac{atoms}{g\ sol.}\right]$	$\frac{Pu-239}{U-238}$ $\left[x\ 10^{-2}\right]$
2	2.944	1.732	0.5883	2.802	1.632	0.5824	2.770	2.081	0.7513
3	2.922	1.713	0.5862	2.794	1.631	0.5838	2.811	2.094	0.7449
4	2.922	(2.644)	-	2.795	(2.261)	-	2.770	(2.206)	-
5	2.928	1.696	0.5792	2.790	1.622	0.5814	2.732	2.129	0.7793
6	2.915	(1.513)	-	2.776	(1.597)	-	2.786	(2.382)	-
7	2.939	1.706	0.5805	2.830	1.632	0.5767	2.770	2.107	0.7606
8	2.955	(2.212)	-	2.809	(1.718)	-	2.747	(2.307)	-
10	2.935	1.695	0.5775	2.787	1.626	0.5834	2.779	2.092	0.7528
12	2.929	1.709	0.5835	2.779	1.632	0.5873	2.781	2.104	0.7566
13	2.911	1.711	0.5878	2.786	1.628	0.5844	2.767	2.103	0.7600
14	2.907	1.706	0.5869	2.791	1.631	0.5844	2.785	2.099	0.7537
15	2.929	1.711	0.5842	2.813	1.637	0.5819	2.747	2.119	0.7714
17	2.959	1.725	0.5830	2.800	1.628	0.5814	2.769	2.096	0.7570
18	2.936	1.704	0.5804	2.818	1.627	0.5774	2.755	2.111	0.7662
19	2.922	1.698	0.5811	2.784	1.619	0.5815	2.770	2.113	0.7628
20	2.941	1.690	0.5746	2.793	1.606	0.5750	2.766	2.118	0.7657
21	2.920	(1.042)	-	2.770	(1.042)	-	2.822	(3.530)	-
23	2.882	-	-	2.737	-	-	2.764	-	-
Mean of means	2.928	1.707	0.5826	2.792	1.627	0.5816	2.772	2.105	0.7602
SD	0.019	0.012	0.0042	0.020	0.008	0.0034	0.021	0.013	0.0091
RSD[%]	0.64	0.69	0.71	0.73	0.48	0.59	0.76	0.62	1.20
						CBNM	2.785	2.109	0.7573

The concentration values were taken from Tables 3-18 and 3-19. For samples A and B the data obtained after "calibration" with sample R were used /Par. 3.5.1/.

Values in brackets were not used for the calculation of mean value, SD and RSD.

3.5.6 Considerations on the Absolute Concentration Values obtained

As actual process sample material was used for the A- and B-solutions, their true U- and Pu-concentrations are unknown. The means of the laboratory means given at the foot of Tables 3-18 and 3-19 for the "calibrated" data can be considered as the "best" values which could be obtained in this experiment. These concentrations in atoms/g solution and the corresponding element concentrations, calculated using the mean isotopic compositions from Tables 3-11 to 3-16 are compiled in Table 3-22 together with those for sample R:

Table 3-22: IDA-72: "Best"-Values for the Uranium and Plutonium Concentrations of the Samples A, B and R

Sample	A ("calibrated")	B ("calibrated")	R	R given by CBNM
Atoms U-238/g sol.	2.928 x 10^{18}	2.792 x 10^{18}	2.772 x 10^{18}	2.785 x 10^{18} ± 0.1%
mg U-element/g sol.	1.1876	1.1324	1.1037	1.1088 ± 0.1%
Atoms Pu-239/g sol.	1.707 x 10^{16}	1.627 x 10^{16}	2.105 x 10^{16}	2.109 x 10^{16} ± 0.1%
µg Pu-element/g sol.	9.473	9.023	8.585	8.599 ± 0.1%

From the data given in this table, the concentration ratio sample A/sample B is calculated to be

$$\frac{2.928}{2.792} = 1.0487$$

or

$$\frac{1.707}{1.627} = 1.0492$$

if it is based on the U-238 or Pu-239 concentration values respectively.

As described in Chapter 2, the two samples were prepared at EUROCHEMIC by dilution of exactly weighed aliquots of about 1.5 ml tank solution with 5 $\underline{M}$ HNO_3 to exactly the same total volume of 262.46 ml.
Therefore, the ratio of the Pu and U concentration of sample A to sample B is given by the weight ratio of the undiluted aliquots , in this experiment

$$\frac{2.2149}{2.0970} = 1.0562$$

This value is 0.7 % higher than the mean of the two ratios calculated above from the concentration measurements. Besides the analytical uncertainties, errors in the dilution and/or the later spiking procedure are possible reasons for this difference. In principle, also inhomogeneity of the tank solution has to be taken into consideration, as the two aliquots were taken from two subsequent samplings. However, as they were performed with a time difference of 5 minutes only and in the middle of a series of 10 samplings, controlled by density determinations showing a maximal difference of 0.07 % (only 0.007 % between the samples from which the aliquotes for the A and B solution were taken), it seems rather improbable that inhomogeneity caused this effect.

Further data on the U- and Pu-concentrations became available by X-ray fluorescence analyses of undiluted process sample material performed at the Institute of Radiochemistry of the GfK, Karlsruhe /Vol. II, Chapter 9/. The mean values of 6 determinations made by this fastmethod which necessitates no chemical pretreatment are given in Table 3-23. For comparison, the data calculated for the undiluted sample solution [1] as the mean from the "calibrated" values of samples A and B obtained in the standard experiment /Tab. 3-22/ and the values of the routine process analysis of EUROCHEMIC [2] are also included in this table. Whereas the agreement of the plutonium values is satisfactory, it is poor for the uranium data. The assumption of evaporation due to radiolysis of the high active undiluted sample material during the storage and transportation time of two weeks could explain the high uranium value obtained by X-ray fluorescence analysis. However, this explanation is not in agreement with the plutonium results which are also confirmed by the process analysis of EUROCHEMIC.

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[1] The data necessary for this calculations are given in Vol. II, Chapter 2

[2] Communicated by R. Berg, EUROCHEMIC, Mol, Belgium, now at GWK, Karlsruhe, Germany

Tab. 3-23: IDA-72: U- and Pu-Concentrations of Undiluted Process Sample Material

Type of analysis	Uranium		Plutonium	
	Concentration [mg/g sol.]	Rel. deviation from standard experiment [%]	Concentration [μg/g sol.]	Rel. deviation from standard experiment [%]
Standard exp.[1]	164.1	-	1310.6	-
X-Ray analysis	166.8	+ 1.6	1309.1	- 0.1
Process analysis EUROCHEMIC	161.7	- 1.5	1305.3	- 0.4

[1] Calculated as mean from "calibrated" values of samples A and B

4. Evaluation of the Self Spike Experiment

4.1 Layout and Participation

In Fig. 4-1 a scheme of the analytical procedure,followed by the laboratories in the self spike experiment,is given and - for comparison - the corresponding part of the standard experiment.

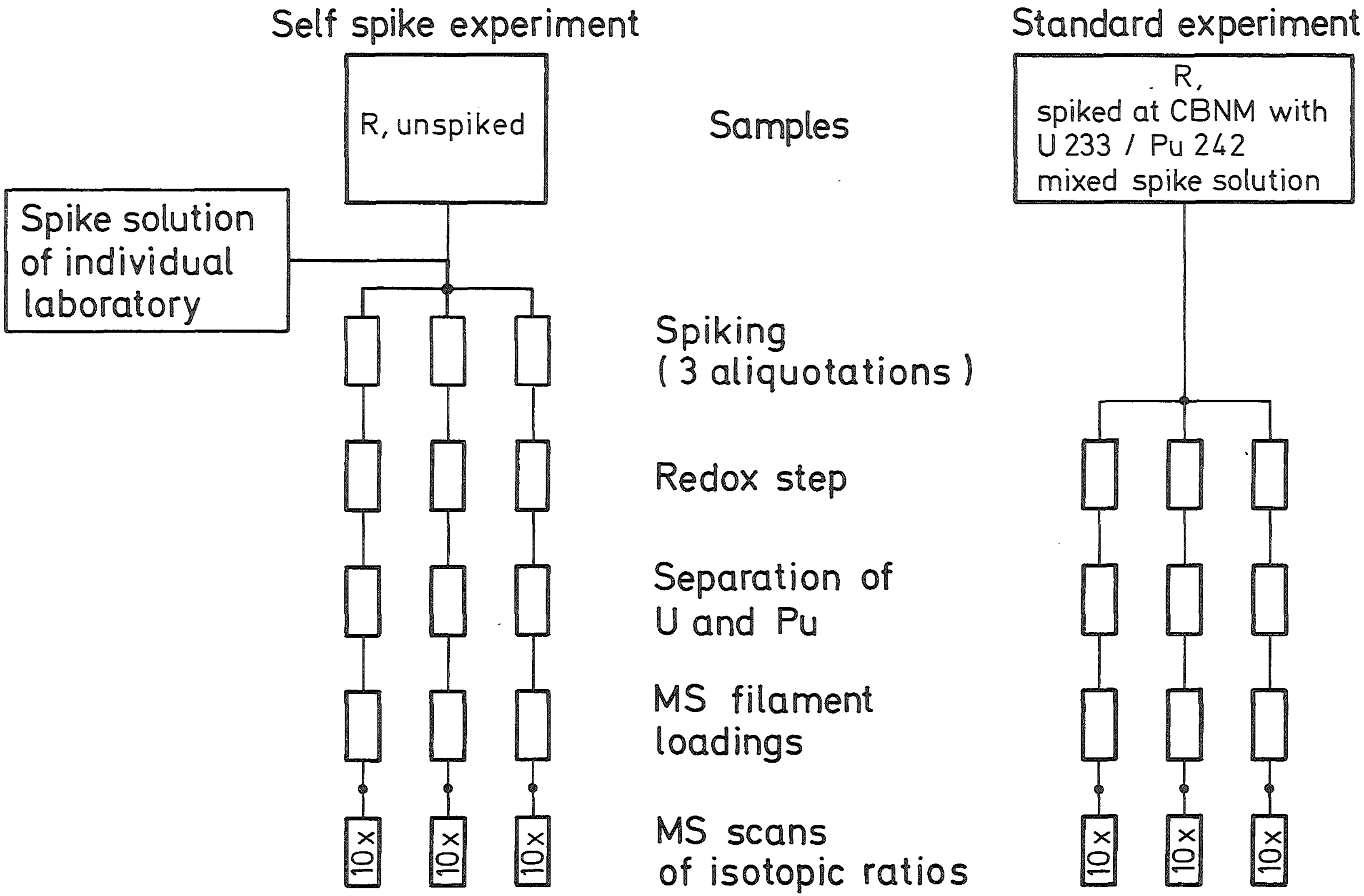
As mentioned above /Par. 2.1/, the synthetical R-solution was used for this test because it was considered as more stable during the time of storage and transportation until spiking in the individual laboratories than the A-and B-solutions,containing fission products.

The sample bottles were carefully weighed at CBNM before their distribution to the laboratories /Vol. II, Par. 3.3.3/. Each laboratory rechecked this weight after the arrival in order to detect eventual losses of sample material by evaporation. Then, each of the laboratories spiked the R-solution in triplicate using its own spike solution. Each of the three samples obtained passed the chemical prepration steps and was measured by one filament loading.

In total, 11 laboratories participated in this test and performed the analyses in accordance with the demands, but with the following exceptions or peculiarities:

Lab. 2	performed two aliquotation only, the second one after quantitative dilution of the unspiked R-solution. Two mass spectrometer runs were made from the material of the second aliquotation.
Lab. 8	performed aliquotations per volume and not per weight. For conversion of data, an experimentally determined value of 1.162 g/ml for the density of the R-solution was used.
Lab. 12	reported the U-233/Pu-242 ratio of its mixed spike solution only, so that only the Pu/U ratio and not the individual element concentrations of the R-sample could be calculated.

Fig. 4-1 IDA-72: Analytical Procedures of the Self Spike Experiment in Comparison to the Corresponding Part of the Standard Experiment



(•) indicate branching points

Lab. 18 Used the isotope Pu-240 as spike. Besides this, also this laboratory diluted the R-solution quantitatively before aliquotation.

4.2 Concentration Determinations

In Table 4-1 all information which was given by the laboratories on their spike solutions is compiled.

Only two laboratories (12 and 17) used mixed U-233/Pu-242 spike solutions. With the exception of the U spike solution used by laboratory 2, the isotopic purity for U-233 was always better than 97%, for Pu-242 better than 90%. In most cases, the spike solutions were calibrated against the NBS-standards 950 and 949. The dates of the last calibrations as reported by the laboratories are given in column 8 and 15 of Table 4-1.

In Tables 4-2 and 4-3 all data which are necessary for the calculation of the U-238 and Pu-239 concentrations of the R-sample solution for the individual laboratories are collected.

In column 2, the reported dates of aliquotation are given. As far as it could be determined, the results were not influenced by the age of the samples.

The U-238 concentrations, calculated on the basis of the formula given for the standard experiment /Par. 3.5.1/ and expressed as number of atoms/g solution are compiled in column 2 of Table 4-4.

The results of the first analysis of laboratory 2 was considered as outlier and rejected from further calculations. The unfavourably small isotopic ratio U-233/U-238 in the spiked sample solution /Tab. 4-2, column 6/ offers an explanation for the deviation of this value.

Tab. 4-1 IDA-72 : Self Spike Experiment/Data Reported on Spike Solutions

Column	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
		Uranium							Plutonium						
			Isotopic composition of spike (atomic ratio)							Isotopic composition of spike (atomic ratio)					
Lab. Code	Type used	Element concentration [mg U/g sol.]	U-234/U-233	U-235/U-233	U-236/U-233	U-238/U-233	Calibrated against standard	Date of last calibration	Element concentration [µg Pu/g sol.]	Pu-238/Pu-242	Pu-239/Pu-242	Pu-240/Pu-242	Pu-241/Pu-242	Calibrated against standard	Date of last calibration
2	U-233,Pu-242 Separate	0.06379 1)	.00100	.00152	.000013	.2060	NBS 950 A	Nov. 72	0.1259 2)	-	.000132	.000344	.000418	Lab.internal Pu metal stand.	Oct. 72
3	U-233,Pu-242 Separate	0.7525	-	-	-	.00055	NBS 960	Sept.72	8.679	-	.000012	-	-	NBS 949 C	Sept. 72
4	U-233,Pu-242 Separate	0.1132	.00246	-	-	.00165	NBS 950 A	March,73	2.173 3)	-	.0358	.0262	.0228	NBS 949 C	March 73
5	U-233,Pu-242 Separate	0.24598	-	-	-	.0043	NBS 950 A	Aug. 72	2.01358	-	.00037	-	-	NBS 949 B	Aug. 72
7	U-233,Pu-242 Separate	0.09818	.0016	.0021	-	.0013	Lab.internal U metal and U_3O_8 stand.	Nov. 72	2.068	-	.0002	.0008	.0008	Lab.internal Pu metal stand.	Nov. 72
8	U-233,Pu-242 Separate	1.201 4)	.01040	.00029	<0.000005	.0217	Lab.internal U metal stand. and NBS 950A	Oct. 72	112.4 3)	-	.0214	.0433	.0285	"Lab.Internal Pu-oxyde stand.	Medio 71
12	U-233,Pu-242 Mixed	not known 5)	.0046	-	-	.00023	not reported	Oct. 69	not known 5)	-	.0261	.0176	.0201	not reported	Oct. 69
13	U-233,Pu-242 Separate	1.0363 1)	.0120	.00042	-	.0042	NBS 950 A	Aug. 72	6.8125 2)	-	.00025	.00083	.00079	NBS 949 B	Aug. 72
15	U-233,Pu-242 Separate	0.4843 1)	.001911	.000695	.000164	.002303	NBS 950 A	Jan. 73	10.24 2)	-	.000313	.000856	.000793	NBS 949 B	Jan. 73
17	U-233,Pu-242 Mixed	1.0177	.00656	.000073	-	.00125	Lab internal U metal stand.	Oct. 72	8.5584	.000037	.00018	.00081	.00081	NBS 949 C	Oct. 72
18	U-233,Pu-240 Separate	0.02970	.000003	.000001	.00001	.000001	NBS 950 A	May, 72	2.456	238/240: .000018	239/240: .00801	241/240: .00614	242/240: .00178	NBS 944	Apr. 72

1) U-233 concentration

2) Pu-242 concentration

3) µg Pu/ml sol.

4) mg U/ml sol.

5) Pu/U ratio determination only.
Spike ratio U-233/Pu-242 = 633.2 ± 1.0

Tab. 4-2 IDA-72: Self Spike Experiment/Basic Data for Calculation of U-238 Concentrations (R-Sample Solution)

Column	1	2	3	4	5	6	7	8	9
Lab. Code	Number of aliquotation	Date of aliquotation	Weight of U-spike aliquote [g]	Weight of R-sample aliquote [g]	U-233 1) concentration of spike solution $\left[\times 10^{18} \frac{\text{atoms}}{\text{g sol.}}\right]$	Ratio 2) $\frac{\text{U-233}}{\text{U-238}}$ of spiked R-solution	Ratio 3) $\frac{\text{U-233}}{\text{U-238}}$ of unspiked R-solution	Ratio 4) $\frac{\text{U-238}}{\text{U-233}}$ of spike solution	Remark
2	1	12.11. 72	.1014	.1024	.16484	.06036	<.00001	.2060	Dilution factor 54.731 5)
	2	2. 1. 73	.0765 5)	.0988 5)		1.672 5)			
	-5)	-	-	-		1.681 5)			
3	1	4.10. 72	2.5093	2.3236	1.9434	.7515	.00004	.00055	-
	2	"	2.5091	2.3262		.7501			
	3	"	2.5091	2.3269		.7529			
4	1	27. 2. 73	2.5762	.2285	.29132	1.193	-	.00165	-
	2	"	2.4780	.2305		1.125			
	3	"	2.5943	.2315		1.197			
5	1	11.10. 72	.9281	.2016	.63248	1.038	-	.0043	-
	2	"	.9130	.2017		1.020			
	3	"	.9216	.1987		1.043			
7	1	4.12. 72	6.2479	1.0001	.25244	.5643	-	.0013	-
	2	"	6.4810	.7749		.7589			
	3	"	6.5712	.8328		.7187			
8	1	11. 9. 72	.5000 6)	.9995 6)	3.0045 8)	.4580	<.00010	.0217	-
	2	"	.5002 6)	.9993 6)		.4594			
	3	"	.5000 6)	.9995 6)		.4556			
12	1	30.11. 72	1. 6)	.25 6)	not known 9)	1.8301	-	.00023	-
	2	"	1. 6)	.25 6)		1.7750			
	3	1.12. 72	1. 6)	.25 6)		1.8227			
13	1	28.11. 72	.7065	.7698	2.6779	.8756	-	.0043	-
	2	"	.7547	.7180		.9987			
	3	"	.7037	.7644		.8763			
15	1	4. 1. 73	.21765	.11324	1.2515	.8676	-	.002303	-
	2	"	.21923	.11591		.8550			
	3	"	.21962	.11610		.8507			
17	1	23.11. 72	.66070	.65525	2.6091	.9529	-	.00125	-
	2	"	.77785	.86065		.8506			
	3	"	1.14160	1.12145		.9592			
18	1	30. 8. 72	11.41952	3.11426 7)	.07675	.9215	-	.000001	Dilution factor 9.01628 7)
	2	"	11.36848	3.10993 7)		.9101			
	3	"	11.33121	3.09754 7)		.9102			

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1) Calculated from data in Tab. 4-1 using the following values for the nuclid masses:

U-233 : 233.0395
U-234 : 234.0409
U-235 : 235.0439
U-236 : 236.0457
U-238 : 238.0508
and L = 6.02205 x 10^{23}/ Mol for Avogadro's number.

2) Run mean value calculated from first 8 scan values after application of Dixon criterion with α = 0.05

3) Value taken from standard experiment.

4) Value taken from Table 4-1, column 7

5) Only two aliqotations performed. For the second one, 0.1087 [g] unspiked R-solution were diluted to 5.9493 [g] with nitric acid and loaded on two mass spectrometer beads.

6) [ml] volume.

7) Before aliquotation, 2.88834 [g] unspiked R-solution were diluted to 26.04207 [g].

8) x 10^{18} atoms/ml solution.

9) Pu/U ratio determination only, Spike ratio U-233/Pu-242 = 633.2 ± 1.0

Tab. 4-3 IDA-72: Self Spike Experiment/Basic Data for Calculation of Pu-239 Concentrations (R-Sample Solution)

Column	1	2	3	4	5	6	7	8	9
Lab. Code	Number of aliquotation	Date of aliquotation	Weight of Pu-spike aliquote [g]	Weight of R-sample aliquote [g]	Pu-242 1) concentration of spike solution $\left[x10^{16} \frac{\text{atoms}}{\text{g sol.}}\right]$	Ratio 2) $\frac{\text{Pu-242}}{\text{Pu-239}}$ of spiked R-solution	Ratio 3) $\frac{\text{Pu-242}}{\text{Pu-239}}$ of unspiked R-solution	Ratio 4) $\frac{\text{Pu-239}}{\text{Pu-242}}$ of spike solution	Remark
2	1	12.11.72	.1014	.1024	.031322	.01474	.000055	.000132	
	2	2. 1.73	.1083 5)	.0988 5)		.8725			Dilution factor 54.731 5)
	-5)	-	-	-		.8763			
3	1	4.10.72	2.4953	2.3236	2.1592	1.092	.000031	.000012	-
	2	"	2.4949	2.3262		1.095			
	3	"	2.4954	2.3269		1.094			
4	1	2. 3.73	1.0 6)	.2595	.49870 10)	1.139	-	.0358	-
	2	"	1.0 6)	.2319		1.017			
	3	"	1.0 6)	.2474		1.102			
5	1	11.10.72	.8660	.2016	.50075	1.147	-	.00037	-
	2	"	.8817	.2017		1.192			
	3	"	.9152	.1987		1.205			
7	1	4.12.72	3.4555	1.0001	.51356	.8454	.000024	.0002	-
	2	"	3.2684	.7749		1.035			
	3	"	3.1905	.8328		.9434			
8	1	11.9. 72	.0999 6)	.9995 6)	25.598 10)	1.075	.00030	.0214	-
	2	"	.1001 6)	.9993 6)		1.064			
	3	"	.0999 6)	.9995 6)		1.088			
12	1	30.11.72	1. 6)	.25 6)	not known 12)	.3767	-	.0261	-
	2	"	1. 6)	.25 6)		.3645			
	3	1.12.72	1. 6)	.25 6)		.3749			
13	1	28.11.72	.9280	.7763	1.6948	.9609	-	.00025	-
	2	"	.9074	.7698		.9479			
	3	"	.9149	.7644		.9616			
15	1	4. 1.73	.21990	.23314	2.5476	2.001	.000050	.000313	-
	2	"	.22131	.23106		2.029			
	3	"	.22137	.23059		2.037			
17	1	23.11.72	.66070	.65525	2.1254	1.021	.000030	.00018	-
	2	"	.77785	.86065		0.9145			
	3	"	1.14160	1.12145		1.031			
18	1	30. 8.72	1.51499	3.11426 7)	.60644 11)	1.276 8)	.0262 8)	.00801 9)	Dilution factor 9.01628 7)
	2	"	1.51405	3.10993 7)		1.271 8)			
	3	"	1.51249	3.09754 7)		1.266 8)			

1) Calculated form data in Tab. 4-1 using the following values for the nuclide masses:

Pu-238 : 238.0495
Pu-239 : 239.0522
Pu-240 : 240.0540
Pu-241 : 241.0567
Pu-242 : 242.0587
and L = 6.02205x 10^{23}/Mol for Avogadro's number.

2) Run mean value calculated from first 8 scan values after application of Dixon criterion with $\alpha = 0.05$

3) Value taken from standard experiment

4) Value taken from Tab. 4-1, Column 11.

5) Only two aliquotations performed. For the second one, 0.1087 [g] unspiked R-solution were diluted to 5.9493 [g] with nitric acid and loaded on two mass spectrometer beads.

6) [ml] volume

7) Before aliquotation, 2.88834 [g] unspiked R-solution were diluted to 26.04207 [g].

8) Ratio Pu-240/Pu-239

9) Ratio Pu-239/Pu-240

10) x 10^{16} atoms/ml sol.

11) Pu-240 concentration of spike solution $\left[x10^{16} \frac{\text{atoms}}{\text{g sol.}}\right]$

12) Pu/U ratio determination only. Spike ratio U-233/Pu-242 = 633.2 ± 1.0

Tab. 4-4 IDA-72: Self Spike Experiment/U-238 Concentration Determination (R-Sample Solution)

Column	1	2	3	4	5	6	7	8
Lab. Code	Number of aliquotation	U-238 1) concentration $\left[\times 10^{18} \frac{\text{atoms}}{\text{g sol.}}\right]$	Lab. mean U-238 concentration $\left[\times 10^{18} \frac{\text{atoms}}{\text{g sol.}}\right]$	RSD of mean [%]	Lab. mean U-238 concentration from standard experiment 2) $\left[\times 10^{18} \frac{\text{atoms}}{\text{g sol.}}\right]$	RSD of mean from standard experiment [%]	Deviation of lab. mean value self spike exp. from that of standard exp. [%]	Change of sample weight during transportation and storage 3) [%]
2	1 2 5) -	(2.671) 4) 2.739 2.717	2.728	.40	2.770	.02	- 1.52	+ .003
3	1 2 3	2.792 2.793 2.782	2.789	.13	2.811	.02	- .78	+ .001
4	1 2 3	2.748 2.779 2.722	2.750	.60	2.770	.29	- .72	- .02
5	1 2 3	2.794 2.796 2.792	2.794	.04	2.732	.09	+ 2.27	- .27
7	1 2 3	2.793 2.779 2.769	2.780	.25	2.770	.21	+ .36	- .007
8	1 2 3	2.796 6) 2.790 6) 2.812 6)	2.799 6)	.23	2.747	.14	+ 1.89	- .18
12	1 2 3	not known 7)			(2.781) 8)	.15	-	± .0
13	1 2 3	2.796 2.806 2.803	2.802	.11	2.767	.04	+ 1.23	-2.3
15	1 2 3	2.767 2.763 2.777	2.769	.15	2.747	.15	+ .80	- .01
17	1 2 3	2.758 2.769 2.766	2.764	.12	2.769	.10	- .18	- .004
18	1 2 3	2.754 2.780 2.781	2.772	.32	2.755	.22	+ .62	- .02
Mean of lab. means			2.775		2.764			
SD			.023		.021			
RSD [%]			.84		.76			

---

1) Calculated from data in Tab. 4-2.

2) Values taken from Tab. 3-21.

3) This is the difference between the sample bottle weight determined at CBNM before shipment and the weight reported by the laboratories. It is given in percents of a sample solution weight of 10 g assumed for all bottles.

4) Value considered as outlier.

5) Second mass spectrometer run with sample material of the second aliquotation.

6) Calculated using a density of 1.162 g/ml, 20°C.

7) Pu/U ratio determination only.

8) Not used for calculation of mean of lab. means as no self spike value is available for this laboratory.

In column 7 of Tab. 4-4 for each laboratory the deviation of its "self-spike experiment mean value" from its "standard experiment mean value" is given, expressed as percentage. In order to study whether or not the higher positive values obtained for the laboratories 5, 8 and 13 could be explained by increase in concentration of the R-sample material due to evaporation losses, the relative changes of the sample weights during transportation and storage are given in column 8 for comparison /Par. 4.1/. It can be noted that the highest negative values are indeed found for the three laboratories mentioned above, but only for laboratory 13 the correlation is also roughly quantitative.

At the foot of Table 4-4 the means of the laboratory means for the U-238 concentrations obtained in the self spike and standard experiment are given in columns 3 and 5, respectively. The mean concentration of the self spike experiment is about 0.4% higher than that calculated from the standard experiment for the same group of laboratories.

A graphical presentation of these results is given in Fig. 4-2. The reference value of CBNM for the U-238 concentration of this R-sample material and the mean concentration value from the measurements of all 18 laboratories which participated in the standard experiment[1] /Fig. 3-35/ are also indicated in this figure.

Table 4-5 and Fig. 4-3 show the results obtained correspondingly for plutonium. As already observed in the standard experiment /Fig. 3-38/ again various outlier values are obtained. The four laboratories concerned (4, 5, 8, 15) specificly rechecked all data, but no proved explanations could be found. Errors in spike solution calibration or, in the case of laboratory 15, interchanged sample material seem to be the most probable reasons. It is remarkable that all outlier concentration values of the self spike experiment are too low, whereas those of the standard experiment are all too high /Fig. 3-38/. However, no plausible explanation could be given for this effect.

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1) It is interesting to note that this value deviates by about 0.3% from the mean value used as reference in Fig. 4-2. In general an uranium concentration mean value based on the measurements of 10 laboratories would probably be considered as very well founded, and one would not expect a change of about 0.3% by adding the results of 8 further laboratories.

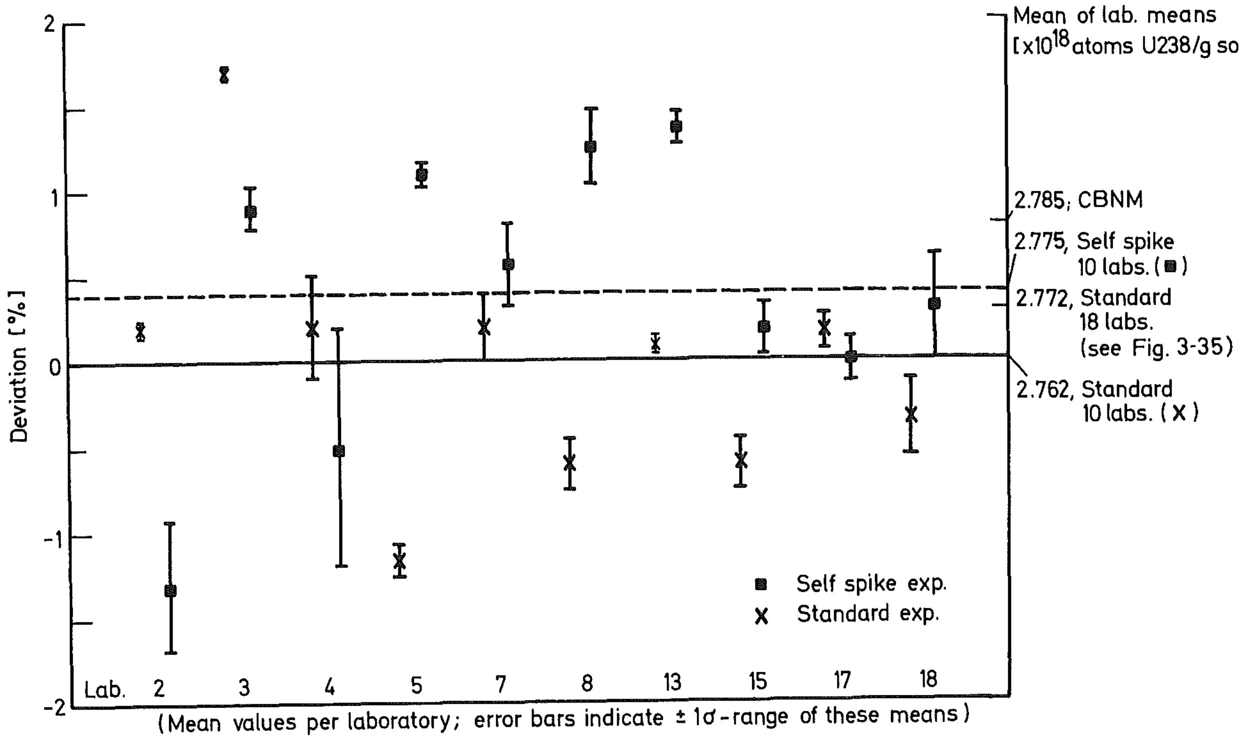

Fig. 4-2 IDA-72 : Self Spike Exp./ U238 - Concentration Determinations (Sample R)

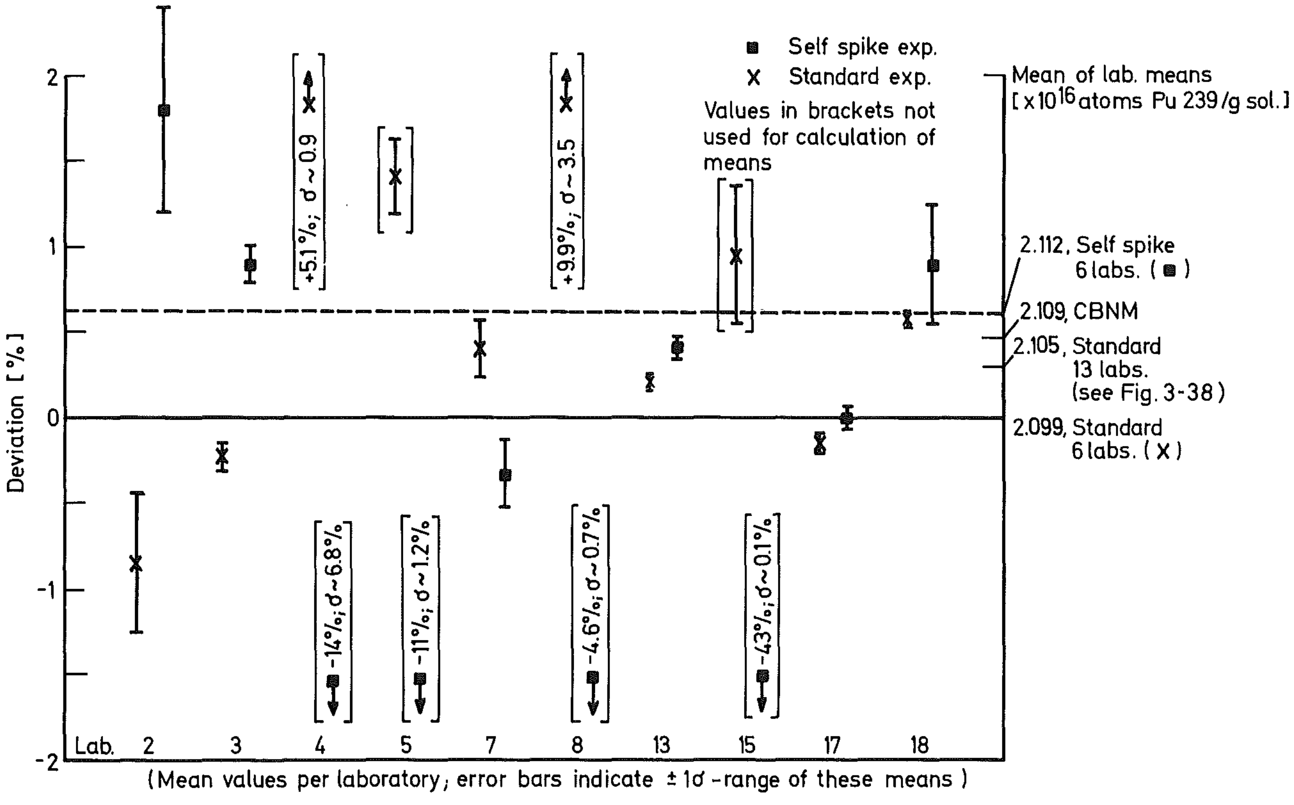

Fig. 4-3 IDA-72: Self Spike Exp./ Pu 239 - Concentration Determinations (Sample R)

Tab. 4-5 IDA-72: Self Spike Experiment/Pu-239 Concentration Determination (R-Sample Solution)

Column	1	2	3	4	5	6	7
Lab. Code	Number of aliquotation	Pu-239 1) concentration $\left[x10^{16}\ \frac{\text{atoms}}{\text{g sol.}}\right]$	Lab. mean Pu-239 concentration $\left[x10^{16}\ \frac{\text{atoms}}{\text{g sol.}}\right]$	RSD of mean [%]	Lab.mean Pu-239 concentration from standard experiment 2) $\left[x10^{16}\ \frac{\text{atoms}}{\text{g sol.}}\right]$	RSD of mean from standard experiment [%]	Deviation of lab. mean value self spike exp. from that of standard exp. [%]
2	1	2.113					
	2	2.154	2.137	.58	2.081	.40	+ 2.69
	-3)	2.144					
3	1	2.123					
	2	2.115	2.118	.11	2.094	.07	+ 1.15
	3	2.117					
4	1	1.618					
	2	2.038	(1.805) 6)	6.84	(2.206) 6)	.89	-
	3	1.758					
5	1	1.875					
	2	1.836	(1.875) 6)	1.20	(2.129) 7)	.22	-
	3	1.913					
7	1	2.099					
	2	2.092	2.092	.19	2.107	.17	- 0.71
	3	2.085					
8	1	2.001 4)					
	2	2.027 4)	(2.002) 4) 6)	.72	(2.307) 6)	3.50	-
	3	1.977					
12	1						
	2	not known 5)			(2.104) 7)	.11	-
	3						
13	1	2.108					
	2	2.107	2.108	.03	2.103	.04	+ 0.24
	3	2.109					
15	1	1.200					
	2	1.202	(1.201) 6)	.06	(2.119) 7)	.38	-
	3	1.200					
17	1	2.099					
	2	2.100	2.099	.03	2.096	.05	+ 0.14
	3	2.098					
18	1	2.106					
	2	2.116	2.118	.34	2.111	.02	+ 0.33
	3	2.131					
Mean of lab. means			2.112		2.099		
SD			.016		.011		
RSD [%]			.76		.51		

---

1) Calculated from data in Tab. 4-3.

2) Values taken from Tab. 3-21.

3) Second mass spectrometer run with sample material of the second aliquotation.

4) Calculated using a density of 1.162 g/ml, 20°C.

5) Pu/U ratio determination only.

6) Value considered as outlier

7) Not used for calculation of mean of lab. means as no self spike value is available for this laboratory.

For calculation of the mean value from the results of the standard experiment, used as reference value in Fig. 4-3 and given at the foot of Table 4-5, in addition to the outlier values (lab. 4 and 8) also the values of the laboratories 5 and 12 were disregarded. This was done, because the values of these laboratories from the self spike experiment are outliers and because it seemed advisable to base any comparison of the self spike and standard experiment results on the values of the same group of laboratories.

It should be noted that for both, uranium and plutonium, the mean values of the self spike experiment are in better agreement with the reference value of CBNM than those of the standard experiment, in the case of plutonium at least if they are based on the same group of laboratories.

In Table 4-6 the Pu-242/U-233 ratios calculated from the laboratory mean values of the self spike experiment are compiled and compared with those of the standard experiment for the same laboratories. In addition to the 6 laboratories, for which Pu-concentration values were available, the ratio determination of laboratory 12 is included, too. At the foot of the table the means of the laboratory means, their standard deviations and relative standard deviations are given. From the self spike experiment higher values are obtained. Comparison of these relative standard deviations with those calculated for the separate determinations of the Pu-239 and U-238 concentrations given in Tables 4-4 and 4-5 shows even more clearly than in the standard experiment /Par. 3.5.5/ that no smaller limits of error can be expected for the Pu/U ratio determinations than for the concentration measurements of the individual elements.

Tab. 4-6 IDA-72 : Self Spike Experiment/
Pu-239/U-238 Concentration Ratios
(R-Sample Solution)

Lab. Code	Atomic ratio $\frac{Pu-239}{U-238}$ from self spike exp. $[\times 10^{-2}]$	Atomic ratio $\frac{Pu-239}{U-238}$ from stand. exp. 1) $[\times 10^{-2}]$	Deviation of lab. mean value self spike exp. from that of standard exp. [%]
2	.7834	.7513	+ 4.27
3	.7594	.7449	+ 1.95
7	.7525	.7606	- 1.06
12	.7609	.7566	+ 0.57
13	.7523	.7600	- 1.01
17	.7594	.7570	+ 0.32
18	.7641	.7662	+ 0.27
Mean of lab. means	.7617	.7567	
SD	.0105	.007	
RSD [%]	1.38	.91	

1) Values taken from Tab. 3-21

4.3 Calculation of Estimates for the Relative Standard Deviations of Error Components

In order to make a quantitative comparison of the error components for the experimental conditions of the standard and self spike experiments possible, estimates for the precision and interlaboratory deviation were calculated by analysis of variances for the two experiments, based on the concentration determinations obtained for the same group of laboratories /Par. 2.5/.

As can be seen in the paragraph above /Par. 4.2/, the data of 10 laboratories could be used in the case of uranium 1), those of 6 laboratories only in the case of plutonium,because 4 laboratories reported outlier values. The results of the calculations are summarized in Table 4-7. For comparison, the corresponding values which were calculated in the standard experiment on the basis of the measurements of all laboratories are given in brackets /Par. 3.5.4/. The agreement is satisfactory in all cases.

Table 4-7: IDA-72: Self Spike Experiment/
Calculated RSD of Error Components for U-238 and
Pu-239 Concentrations Determinations (R-Sample Solution)

Isotope	Precision RSD [%]		Interlab. deviation RSD [%]		Number of laboratories and single determinations on which calculations were based	
	self spike exp.	standard exp.	self spike exp.	standard exp.	self spike exp.	standard exp.
U-238	0.47	0.27 (0.29)	0.74	0.75 (0.75)	10/29 1)	10/30 (18/54)
Pu-239	0.51	0.31 (0.38)	0.70	0.49 (0.59)	6/18	6/18 (13/39)

For comparison the values calculated in the standard experiment cf. Table 3-20 /Par. 3.5.4/ are given in brackets.

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1) The result obtained by laboratory 2 from the first aliquotation was not considered.

In the following, an attempt is made for a more detailed interpretation of these results:

Compared to the conditions of the standard experiment, in the self spike experiment the spiking procedure represents an additional error source. According to the experimental layout of the self spike experiment /Fig. 4-1/ and the structure of the variance analysis/ Par. 2.5 /, the error of the spiking procedure is split into two components: One component, which can be understood e.g. as the error of the aliquotation procedure, is different for each single analysis and, therefore, contributes to the precision. The other component, which can be understood e.g. as the error in the calibration of the spike solution, is constant for all measurements performed within one individual laboratory, but different from one laboratory to the other and, therefore, contributes to the interlaboratory deviation.

The variance for the additional "aliquotation error component" is given as the difference of the variances for the precision error component in the self spike and standard experiment. Expressed as relative standard deviation (in percent) from the data given in Tab. 4-7, the values

$$\sqrt{0.47^2 - 0.27^2} = 0.38 \qquad \text{for uranium}$$

and

$$\sqrt{0.51^2 - 0.31^2} = 0.40 \qquad \text{for plutonium}$$

are obtained. This means approximately the same magnitude of 0.4 % for both, uranium and plutonium, which would be in agreement with the interpretation of this error component as caused by the aliquotation procedure.

A corresponding calculation for the interlaboratory deviation based on the data of Tab. 4-7 leads to the values

$$\sqrt{0.74^2 - 0.75^2} \approx 0.0 \qquad \text{for uranium}$$

and

$$\sqrt{0.70^2 - 0.49^2} = 0.50 \qquad \text{for plutonium.}$$

In the case of uranium, this result looks like there is no additional error contribution by the spiking procedure, although this is certainly the case e.g. due to errors in the spike solution concentrations used by the individual laboratories. This contradiction can be dissolved by the assumption of an error component being present in the case of the standard experiment but not existing or, more likely, being compensated in the procedure followed in the self spike experiment.

As already mentioned in the evaluation of the standard experiment /Par. 3.1/, the mass discrimination has this characteristic and should be more significant for uranium than for plutonium [1]. This is in agreement with the results given in Tab. 4-7. There is the objection that all laboratories applied mass discrimination corrections to their isotopic ratio determinations /Vol. II, Chapter 7/ and that therefore the results of the standard experiment should be unaffected by this effect. However, this is not confirmed by the reults obtained in the standard experiment:
In spite of the mass discrimination corrections, the interlaboratory deviations calculated from the measurements on the A- and B-sample material are reduced, if a further laboratory internal correction is applied by "calibration" with the R-sample solution /Par. 3.5.1/. This change in the interlaboratory deviation is more significant for uranium than for plutonium /Tab. 3-20/. This can only be understood if the corrections applied by the individual laboratories were insufficient to correct the mass discrimination completely as stated by the analysts in the IDA-meeting /Par. 8.3.3/ or, as another possibility that there exists a further error source besides mass discrimination in the standard experiment which is also compensated (or not existing) if the self spike procedure is followed.

---

[1] There is a difference of five mass units between the spike isotope (U-233) and the reference sample isotope (U-238) in the case of uranium, but of three mass units only for plutonium (Pu-242, Pu-239).

It is difficult to judge the confidence of the figures calculated for the error components of the spiking procedure in this paragraph. As they are determined by the differences of the estimates for the variances calculated for standard and self spike experiment, some information can be obtained by calculating the confidence limits of these estimates for the variances themselves. As the system is nearly completely orthogonal [1], this is at least possible for the precision. It is found that the confidence limits become small enough to avoid overlapping of the ranges calculated for the variances of standard and self spike experiment, if a probability of error of at least 20% is allowed.

Unfortunately, for statistical reasons no corresponding calculation can be made for the variances of interlaboratory deviation alone, but only for the ratio of the variances of interlaboratory deviation and precision. From such a consideration, however, no clear statements can be deduced.

4.4 Compilation of Basic Data for Calculating Estimates of Total Errors in Isotope Dilution Analysis

From the estimates for the variances of the individual error components obtained in the standard and self spike experiment, the estimate for the total variance of an isotope dilution analysis can be calculated.

The numerical values calculated for the individual error components in terms of relative standard deviations are summarized in Table 4-8. All values for "inactive sample solution" - which means without fission products- were taken from the evaluation of the self spike experiment /Tab. 4-7/, the data for "active sample solution without spiking procedure" are the mean values calculated from the measurements of the A- and B-sample solutions in the standard experiment /Tab. 3-20/. From the latter, the values including the spiking procedure were obtained by correction with the additional spiking error components calculated above /Par. 4.3/.

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[1] The only exception is one missing single uranium determination of lab. 2.

Table 4-8: IDA-72: Compilation of Calculated Error Components for U-238 and Pu-239 Concentration Determinations

Analysed element	Type of sample solution	Including spiking procedure	RSD of precision δ_P [%]	RSD of Interlab. deviation [%]	Calculated after rejection of outliers [%]
Uranium	inactive	no	0.29	0.75	0.0
		yes	0.47	0.74	0.0
	active	no	0.51	0.82	0.0
		yes	0.64	0.82	0.0
Plutonium	inactive	no	0.38	0.59	23.5
		yes	0.51	0.70	40.0
	active	no	0.59	0.53	17.6
		yes	0.71	0.73	not defined

In general, the correlations between the values are meaningful. It has to be emphasized, however, that the data for plutonium were obtained after the rejection of a considerable number of outliers as indicated in the last column of the table.

In the following an example for calculating estimates of total errors from these data is given:
If the result of a concentration determination was obtained as the mean value of $\ell \cdot m$ single determinations performed in such a way that each of ℓ laboratories made m repetition analyses, the relative standard deviation δ_T of the total error of this mean value is given by

$$\delta_T = \left(\frac{\delta^2_{I\,D}}{\ell} + \frac{\delta^2_P}{\ell \cdot m} \right)^{\frac{1}{2}}$$

with

$\delta_{I\,D}$ = RSD of the interlaboratory deviation error component and

δ_P = RSD of the precision error component.

For the common practical case that a concentration value was obtained on a diluted active feed solution by double analysis of one laboratory (including the spiking procedure), one obtaines for its relative standard deviation in the case of uranium with

$\delta_{I\,D}$ = 0.82% and δ_P = 0.64% from the formula given before δ_T = 0.94%,

in the case of plutonium with $\delta_{I\,D}$ = 073% and δ_P = 0.71% one gets δ_T = 0.89%.

This, however, is only correct for U-238 and Pu-239 concentrations. If, as usual, element concentrations are calculated, it can be estimated on the basis of the results discussed in the standard experiment /Tab. 3-20/ that this error is increased in the case of plutonium by about 0.15%. So, if element concentrations are considered, approximately 0.9% are found for uranium and about 1.0% for plutonium - presuming that no outlier values are involved. If the spiking procedure is excluded - as in the standard experiment - the value for plutonium decreases by about 0.2%. For uranium, it remains unchanged.

5. Investigations on New Techniques of Sample Conditioning

5.1 The Dry Spike Experiment

5.1.1 Layout and Participation

As already discussed /Par. 2.1/, this part of the IDA-experiment was planned to prove the capability of the "dry spike" sampling technique which was proposed by the IAEA /Vol. II, Chapt. 4/.

A scheme of the analytical procedures followed by the laboratories is given in Fig. 5-1, which is also valid for part I of the aluminium-capsule experiment described in the next paragraph /Par. 5.2/. For comparison, this figure also shows the corresponding part of the standard experiment.

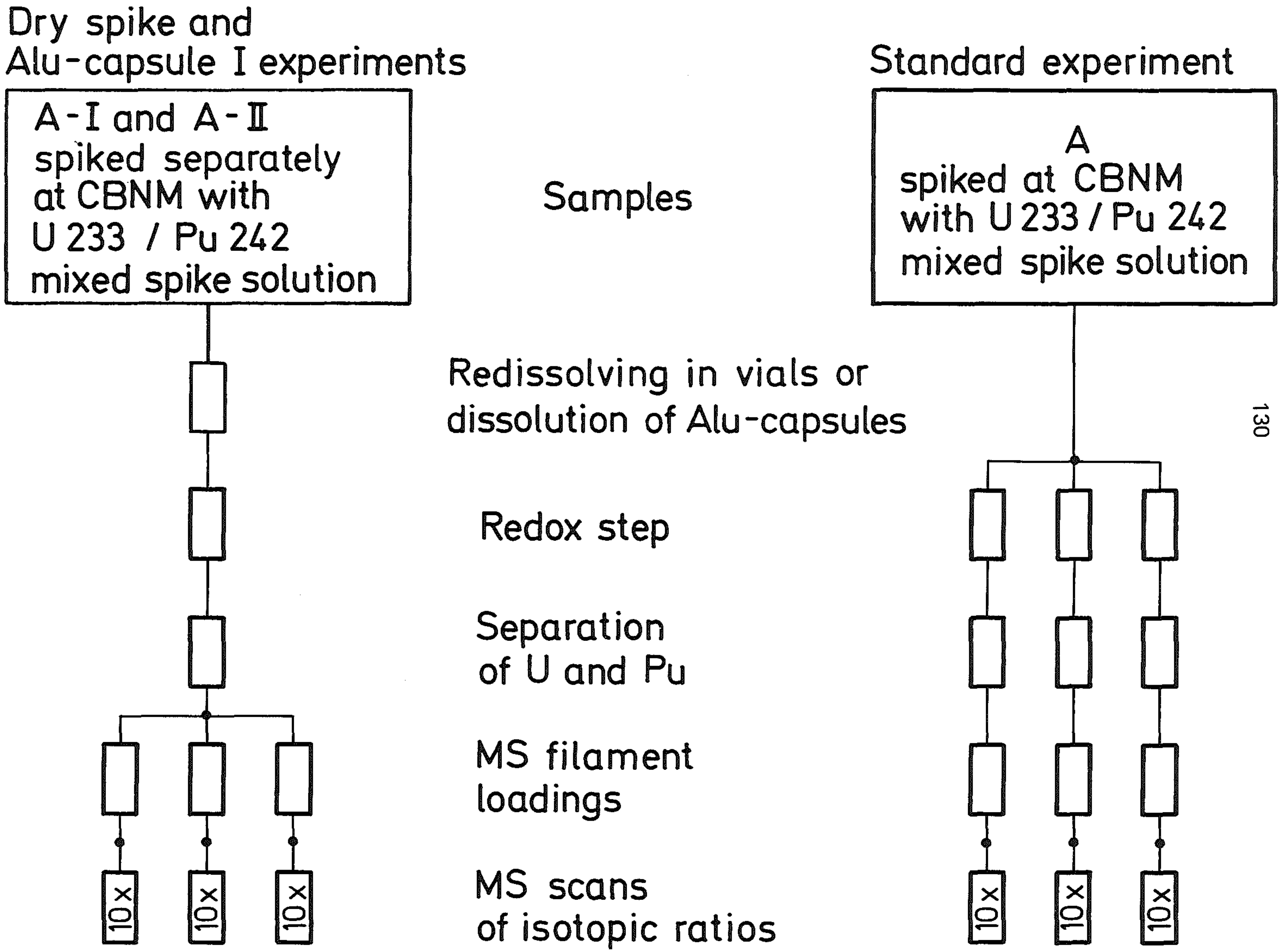
Eight laboratories participated in this test. Each of them obtained two glass sample vials marked "A-I" and "A-II". They were prepared in the laboratories of CBNM-in collaboration with representatives of IAEA-by consecutive evaporation to dryness of a mixed spike aliquot and, afterwards, an aliquot of the A-sample solution /Vol.II,Par.3.3.1 and Vol.II,Chapt.4/. The laboratories redissolved these samples by heating with nitric acid, passed them through the usual sample preparation steps and performed three mass spectrometer runs (three filament loadings) from each of the two samples.

5.1.2 Concentration Determinations

In Table 5-1 all basic data necessary for the calculation of the U-238 and Pu-239 concentrations of the A-samples, as determined by the individual laboratories, are compiled. The aliquot weights given in columns 3 and 4 were unknown to the laboratories at the time of analysis.

The U-238 and Pu-239 concentrations, calculated with the formula discussed in the standard experiment /Par. 3.5.1/ and expressed as number of atoms/g solution, are given in column 3 of Tables 5-2 and 5-3 for each run. In column 4 the mean values per sample and laboratory are shown.

Fig. 5-1: IDA-72: Analytical Procedures of the Dry Spike and Alu-Capsule I Experiment in Comparison to the Corresponding Part of the Standard Experiment



(•) indicate branching points

In order to reduce the interference by error contributions which are not specific for the technique of sample conditioning under investigation, it seemed advisable to "calibrate" all concentration values as explained in the standard experiment /Par. 3.5.1/ with the laboratory mean values of the R-sample solution /Tab. 3-18 and 3-19/. These "calibrated" concentration values are given in column 6 of the tables, the corresponding laboratory mean values obtained on the A-solution in the standard experiment /Tab. 3-18 and 3-19/ in column 7. In case of the Pu-239 concentration determinations, no "calibrated" values can be calculated for the results of the laboratories 6 and 12, because the respective concentration values obtained in the standard experiment on the R-solution were outliers /Tab. 3-19/.

The calculated relative differences between the results of the dry spike and standard experiment for each sample are shown in column 9 of Tables 5-2 and 5-3.

As far as the relative standard deviations of the sample means (dry spike experiment) and laboratory means (standard experiment) are concerned which are given in columns 5 and 8 of the same tables, it should be noted that they are not directly comparable because of the different structure of the two parts of the experiment: Those of the dry spike experiment describe only the variances of the mass spectrometric measurements, whereas in case of the standard experiment they contain also contributions of the chemical sample preparation steps /Fig. 5-1/. Therefore, in general, the latter values should be higher, which is not always the case.

At the foot of the Tables 5-2 and 5-3 the means of the sample means (dry spike experiment) and laboratory means (standard experiment) are given as well as the standard deviation and relative standard deviation of the single sample and of the single laboratory mean, respectively: Comparison of the mean of the means gives no indication that any systematic error is introduced by the dry spike technique. This allows to conclude that the redissolved mixture of spike and sample solution was representative in respect to its isotopic composition /Par. 2.1/.

Tab. 5-1: IDA-72 : Dry Spike Experiment/Basic Data for Calculation of U-238 and Pu-239 Concentrations (A-Sample Solution)

Column	1	2	3	4	5	6	7	8	9	10	11	12
					Uranium				Plutonium			
Lab. Code	Sample	Vial No.	Weight of mixed spike aliquot [g]	Weight of A-sample aliquot [g]	Ratio $\frac{U-233}{U-238}$ of unspiked A-solution[1]	Ratio $\frac{U-238}{U-233}$ of spike solution[1]	Number of MS run	Ratio $\frac{U-233}{U-238}$ of spiked A-solution	Ratio $\frac{Pu-242}{Pu-239}$ of unspiked A-solution[1]	Ratio $\frac{Pu-239}{Pu-242}$ of spike solution[1]	Number of MS run	Ratio $\frac{Pu-242}{Pu-239}$ of spiked A-solution
3	A-I	120	1.16850	1.38737	-	.0225	1	.5845	.0231	.0133	1	1.2257
							2	.5867			2	1.2254
							3	.5875			3	1.2229
	A-II	121	1.16379	1.39530	"	"	1	.5842	"	"	1	1.2143
							2	.5808			2	1.2186
							3	.5815			3	1.2188
6	A-I	118	1.17160	1.39680	-	.0221	1	.5963	.0231	.0133	1	1.2101
							2	.5956			2	1.2097
							3	.5955			3	1.2119
	A-II	119	1.16955	1.40023	"	"	1	.5908	"	"	1	1.2113
							2	.5926			2	1.2086
							3	.5934			3	1.2105
13	A-I	122	1.17084	1.39145	-	.0221	1	.5965	.0226	.0133	1	1.2137
							2	.5989			2	1.2119
							3	.5960			3	1.2126
	A-II	123	1.16509	1.39888	"	"	1	.5925	"	"	1	1.2032
							2	.5923			2	1.2011
							3	.5898			3	1.2052
14	A-I	128	1.16400	1.39505	-	.0222	1	.5868	.0228	.0133	1	1.2092
							2	.5880			2	1.2106
							3	.5892			3	1.2098
	A-II	129	1.17510	1.38875	"	"	1	.5954	'"	"	1	1.2276
							2	.5966			2	1.2261
							3	.5970			3	1.2258
15	A-I	116	1.16943	1.40148	-	.0219	1	.5937	.0231	.0133	1	1.1990
							2	.5943			2	1.1981
							3	.5935			3	1.1949
	A-II	117	1.16009	1.39715	"	"	1	.5914	"	"	1	1.1891
							2	.5931			2	1.1916
							3	.5892			3	1.1961
17	A-I	126	1.16938	1.38902	-	.0223	1	.5961	.0228	.0133	1	1.2188
							2	.5930			2	1.2150
							3	.5970			3	1.2174
	A-II	127	1.16734	1.38355	"	"	1	.5957	"	"	1	1.2159
							2	.5975			2	1.2174
							3	.5953			3	1.2168
18	A-I	124	1.16705	1.39255	-	.0220	1	.5952	.0230	.0133	1	1.2027
							2	.5938			2	1.2076
							3	.5876			3	1.2031
	A-II	125	1.16795	1.39925	"	"	1	.5981	"	"	1	1.1979
							2	.5957			2	1.2017
							3	.5950			3	1.1941
21	A-I	112	1.46135	1.41295	-	.0231	1	.5819	.0242	.0133	1	1.1794
							2	.5813			2	1.1793
							3	.5818			3	1.1800
	A-II	113	1.16986	1.40089	"	"	1	.5881	"	"	1	1.1998
							2	.5885			2	1.1990
							3	.5888			3	1.1993

[1] Values taken from standard experiment /Vol. II, Par. 12.3/.

Tab. 5-2: IDA-72 : Dry Spike Experiment/U-238 Concentration Determination (A-Sample Solution)

Column	1	2	3	4	5	6	7	8	9
Lab. Code	Sample	Number of MS run	U-238 concentration $\left[x10^{18} \frac{atoms}{g\ sol.}\right]$	Mean concentration U-238 per sample $\left[x10^{18} \frac{atoms}{g\ sol.}\right]$	RSD of mean[1] [%]	Mean concentration U-238 per sample "calibrated" with sample R[2] $\left[x10^{18} \frac{atoms}{g\ sol.}\right]$	Lab. mean U-238 concentration standard exp. "calibrated" with sample R[2] $\left[x10^{18} \frac{atoms}{g\ sol.}\right]$	RSD of mean from stand. exp.[1] [%]	Deviation of mean value of dry spike exp from that of standard exp. [%]
3	A-I	1	2.976						
		2	2.965	2.968	.15	2.941			+ .65
		3	2.961						
	A-II	1	2.949				2.922	.13	
		2	2.967	2.960	.18	2.933			+ .38
		3	2.963						
6	A-I	1	2.905						
		2	2.909	2.908	.05	2.907			- .27
		3	2.910						
	A-II	1	2.921				2.915	.28	
		2	2.912	2.913	.13	2.912			- .10
		3	2.908						
13	A-I	1	2.914						
		2	2.902	2.911	.15	2.930			+ .65
		3	2.917						
	A-II	1	2.904				2.911	.03	
		2	2.905	2.909	.15	2.928			+ .58
		3	2.918						
14	A-I	1	2.938						
		2	2.930	2.931	.12	2.931			+ .83
		3	2.925						
	A-II	1	2.935				2.907	.20	
		2	2.930	2.931	.08	2.931			+ .83
		3	2.928						
15	A-I	1	2.904						
		2	2.901	2.903	.04	2.943			+ .48
		3	2.905						
	A-II	1	2.901				2.929	.32	
		2	2.892	2.902	.19	2.942			+ .44
		3	2.912						
17	A-I	1	2.917						
		2	2.932	2.921	.20	2.938			- .71
		3	2.912						
	A-II	1	2.925				2.959	.37	
		2	2.916	2.923	.11	2.940			- .64
		3	2.927						
18	A-I	1	2.909						
		2	2.916	2.924	.40	2.954			+ .61
		3	2.947						
	A-II	1	2.883				2.936	.32	
		2	2.895	2.892	.16	2.921			- .51
		3	2.898						
21	A-I	1	2.917						
		2	2.920	2.918	.02	2.880			- 1.37
		3	2.918						
	A-II	1	2.932				2.920	.04	
		2	2.930	2.930	.04	2.892			- .96
		3	2.928						
				Mean of means		2.926 (2.932) [3]	2.925		
				SD		.020 (.013) [3]	.017		
				RSD [%]		.68 (.43) [3]	.57		

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[1] The relative standard deviations given in columns 5 and 8 are not directly comparable because of different layout of analytical steps.

[2] For explanation and data see Par. 3.5.1 and Table 3-18

[3] Values in brackets are obtained if data of lab. 21 are disregarded.

Tab. 5-3: IDA-72 ; Dry Spike Experiment/Pu-239 Concentration Determination (A-Sample Solution)

Column	1	2	3	4	5	6	7	8	9
Lab. Code	Sample	Number of MS run	Pu-239 concentration [x10^{16} atoms/g sol.]	Mean concentration Pu-239 per sample [x10^{16} atoms/g sol.]	RSD of mean [%]	Mean concentration Pu-239 per sample "calibrated" with sample R$^{2)}$ [x10^{16} atoms/g sol.]	Lab. mean Pu-239 concentration standard exp. "calibrated" with sample R$^{2)}$ [x10^{16} atoms/g sol.]	RSD of mean from stand. exp. $^{1)}$ [%]	Deviation of mean value of dry spike exp. from that of stand. exp. [%]
3	A-I	1	1.694	1.696	.07	1.708	1.713	.07	- .29
		2	1.695						
		3	1.698						
	A-II	1	1.694	1.690	.12	1.702			- .64
		2	1.688						
		3	1.688						
6	A-I	1	1.710	1.709	.05	-$^{3)}$	-$^{3)}$	.33	-$^{3)}$
		2	1.710						
		3	1.707						
	A-II	1	1.701	1.703	.07	-$^{3)}$			-$^{3)}$
		2	1.705						
		3	1.702						
13	A-I	1	1.709	1.711	.04	1.716	1.711	.01	+ .29
		2	1.712						
		3	1.711						
	A-II	1	1.707	1.707	.10	1.712			+ .06
		2	1.710						
		3	1.704						
14	A-I	1	1.702	1.701	.03	1.709	1.706	.08	+ .18
		2	1.700						
		3	1.701						
	A-II	1	1.699	1.700	.04	1.708			+ .12
		2	1.701						
		3	1.701						
15	A-I	1	1.717	1.720	.10	1.712	1.711	.24	+ .06
		2	1.718						
		3	1.723						
	A-II	1	1.723	1.719	.17	1.711			± .0
			1.713						
17	A-I	1	1.703	1.706	.09	1.717	1.725	.14	- .46
		2	1.709						
		3	1.705						
	A-II	1	1.711	1.710	.04	1.721			- .23
		2	1.709						
		3	1.710						
18	A-I	1	1.719	1.716	.13	1.714	1.704	.04	+ .59
		2	1.712						
		3	1.718						
	A-II	1	1.719	1.719	.18	1.717			+ .76
		2	1.714						
		3	1.725						
21	A-I	1	1.722	1.722	.02	-$^{3)}$	-$^{3)}$	.23	-$^{3)}$
		2	1.722						
		3	1.721						
	A-II	1	1.719	1.720	.02	-$^{3)}$			-$^{3)}$
		2	1.720						
		3	1.720						
				Mean of means		1.712	1.712		
				SD		.005	.007		
				RSD [%]		.30	.43		

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1) The relative standard deviations given in columns 5 and 8 are not directly comparable because of different layout of analytical steps.

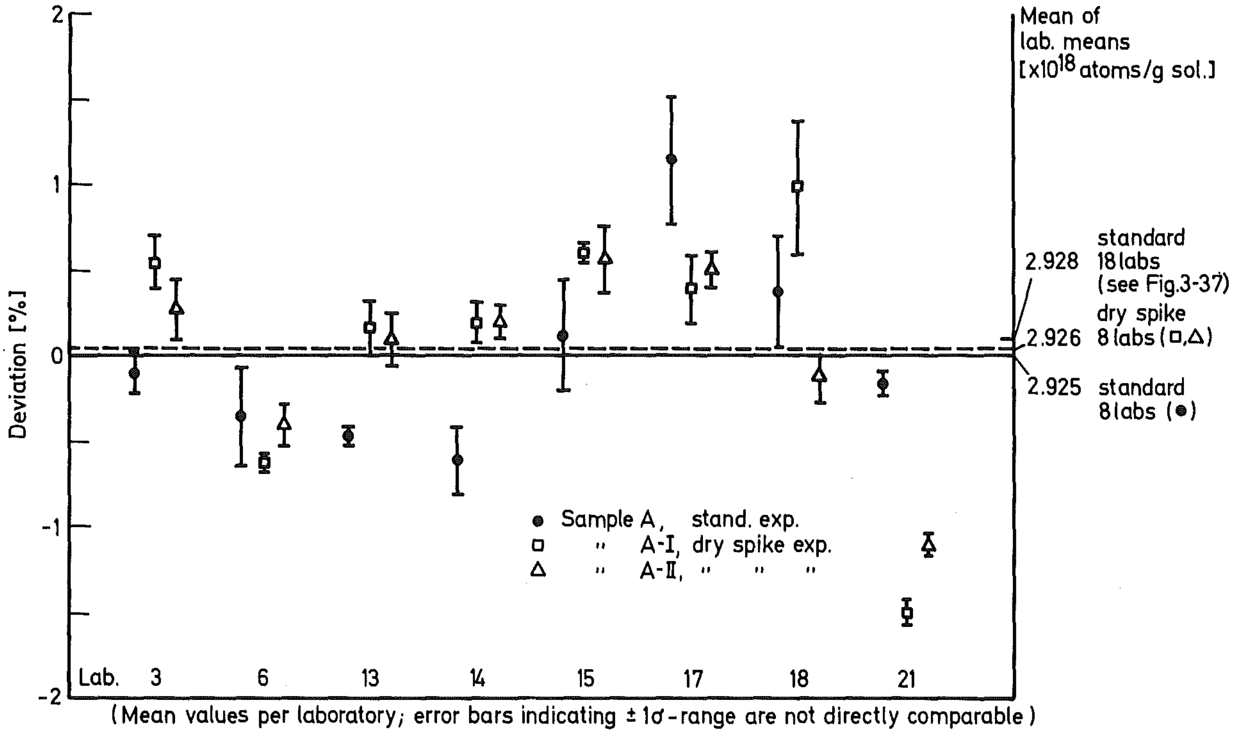
2) For explanation and data see Par. 3.5.1 and Table 3-19.

3) No meaningful values can be given, as the concentration value obtained in the standard experiment on the R-solution was an outlier.

Furthermore a comparison of the standard deviations indicates that they are certainly not significantly higher for the dry spike sample technique. As these standard deviations represent mainly the interlaboratory deviation, this observation is remarkable. It demonstrates that there is no significant error contribution by the individual aliquotation procedure for each vial.

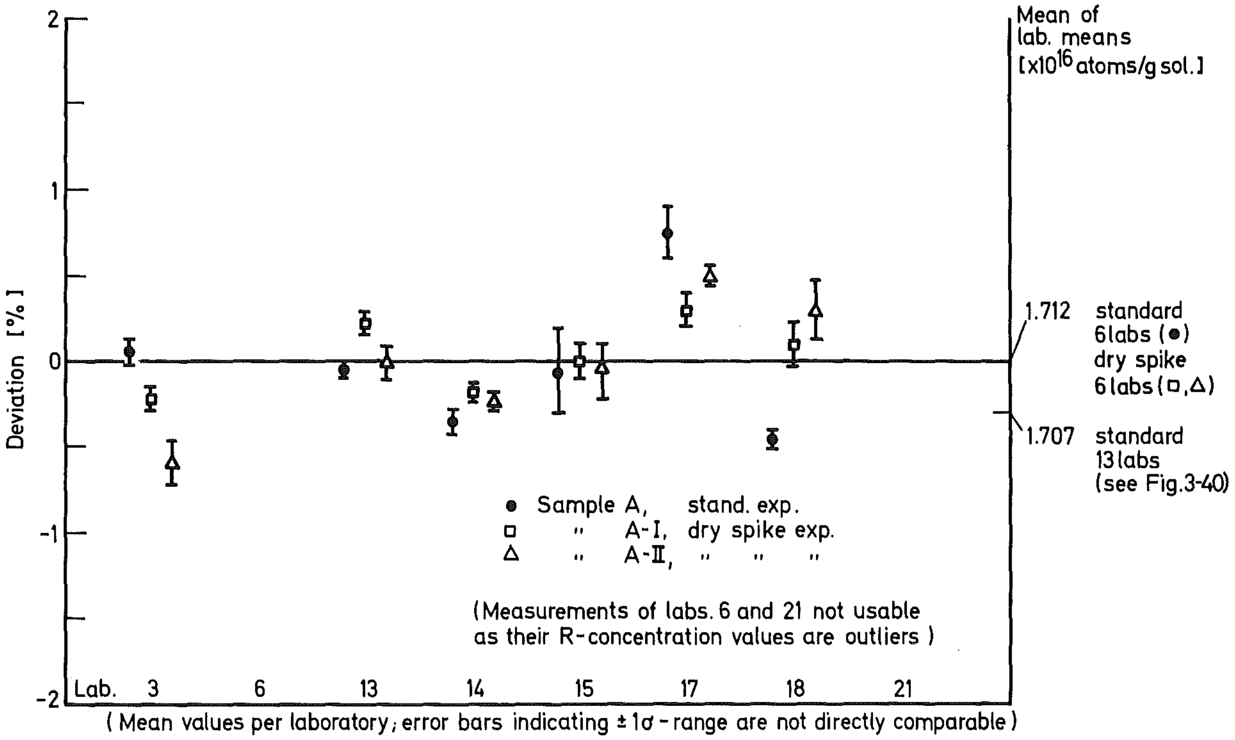
A graphical presentation of these results is given in Figures 5-2 and 5-3. The mean values calculated from the "calibrated" data obtained in the standard experiment by those laboratories which participated in this test were taken as reference values. As mentioned above, the measurements of laboratory 6 and laboratory 21 could not be used in the case of plutonium, as the concentration determinations of the R-solution, needed for calculating the "calibrated" values, were outliers. In the figures, also the mean values for the "calibrated" A-sample calculated on the basis of the measurements of all participants in the standard experiment /Fig. 3-37 and 3-40/ are indicated.

Finally, in Table 5-4 the Pu-239/U-238 ratios calculated from the data of the dry spike experiment are compiled, together with the values from the standard experiment. Comparison of the relative standard deviations, given at the foot of the table, with the corresponding values calculated for the concentration determinations of the individual elements (given at the foot of Tables 5-2 and 5-3) again shows no indication that smaller limits of error can be expected for Pu/U ratio determinations in agreement with the observations in the standard experiment /Par. 3.5.5/ and self spike experiment /Par. 4.2/.



(Mean values per laboratory; error bars indicating ± 1σ-range are not directly comparable)

Fig.5-2 IDA-72 : Dry Spike Exp./U238-Concentration of Samples A-I and A-II in Comparison with Sample A of Standard Experiment (All Values "Calibrated" with Sample R)



(Mean values per laboratory; error bars indicating ± 1σ-range are not directly comparable)

Fig.5-3 IDA-72: Dry Spike Exp./Pu 239-Concentration of Samples A-I and A-II in Comparison with Sample A of Standard Experiment (All Values "Calibrated" with Sample R)

Tab. 5-4: IDA-72: Dry Spike Experiment; Pu-239/U-238 Concentration Ratios (A-Sample Solution)

Column	1	2	3	4
Lab. Code	Sample	Atomic ratio $\frac{\text{Pu-239}}{\text{U -238}}$ from dry spike exp. $[\text{x}10^{-2}]$	Atomic ratio $\frac{\text{Pu-239}}{\text{U -238}}$ from stand. exp. $[\text{x}10^{-2}]$	Deviation of lab.mean value of dry spike exp. from that of stand. exp. [%]
3	A-I	.5808	.5862	-0.92
	A-II	.5803		-1.01
6	A-I	-1)	-1)	-1)
	A-II			
13	A-I	.5857	.5878	- .36
	A-II	.5847		- .53
14	A-I	.5831	.5869	- .65
	A-II	.5827		- .72
15	A-I	.5817	.5842	- .43
	A-II	.5816		- .45
17	A-I	.5844	.5830	+ .29
	A-II	.5854		+ .41
18	A-I	.5802	.5804	- .03
	A-II	.5878		+1.27
21	A-I	-1)	-1)	-1)
	A-II			
Mean of means		.5832	.5848	
SD		.0024	.0028	
RSD[%]		.41	.47	

All data calculated from "calibrated" values.

1) No meaningful "calibrated" Pu-239 concentration value available, as determination on R-solution in the standard experiment was an outlier /Tab. 3-19/.

5.2 The Aluminium-Capsule Experiment, Part I

5.2.1 Layout and Participation

As mentioned before /Par. 2.1/, it was the objective of the aluminium-capsule experiments to prove a sampling technique which was proposed by the Transuranium Institute of EURATOM /Vol. II, Chapt. 5/. Unlike the case of the dry spike experiment /Par. 5.1/, aliquots of mixed spike and A-sample solution were given in aluminium-capsules instead of glass vials, and again one after the other evaporated to dryness. The individual laboratories dissolved the complete capsules in nitric acid.

The layout of part I of this study, which is described in this paragraph, was analogous to that of the dry spike experiment /Fig. 5-1/: two capsules, marked "A-I" and "A-II", were prepared for each of the participating laboratories at CBNM in collaboration with representatives of the Transuranium Institute /Vol. II, Par. 3.3.2 and Vol. II, Chapt. 5/.After dissolution, each laboratory passed them through the usual sample preparation steps and performed three mass spectrometer runs (three filament loadings) from each of the two samples.

The data of six laboratories were available for the evaluation. On the A-II sample, only two plutonium determinations instead of three were reported by laboratory 6.

Laboratory 14, which also intended to participate, reported no values because of difficulties in the chemical separation procedure due to the high ratio Al/(U+Pu).

5.2.2 Concentration Determinations

The evaluation of this part of the experiment was made as already described in the dry spike experiment /Par. 5.1.2/. The basic data necessary for the calculation of the U-238 and Pu-239 concentrations of the A-samples as determined by the individual laboratories are compiled in Table 5-5. The aliquot weights given in columns 3 and 4 were unknown to the laboratories at the time of analysis.

The calculated concentration values are given in Tables 5-6. and 5-7 for U-238 and Pu-239, respectively, together with the data from the standard experiment for comparison.

The values obtained by laboratory 6 on the A-II sample have to be considered as outliers for both, uranium and plutonium, concentrations. It remains open whether this errror was caused during the aliquotation procedure or during dissolution of the capsule and sample handling in the laboratory concerned. In the case of plutonium also no "calibrated" values could be calculated for this laboratory, as the concentration determination of the R-solution was an outlier /Table 3-19/.

As in the case of the dry spike experiment /Par. 5.1.2/, in general higher values should be expected for the relative standard deviations given in column 8 of these tables compared to those compiled in column 5 because of the difference in the structure of the analytical steps in the standard and aluminium-capsule experiments /Fig. 5-1/. However, this is not confirmed in all cases.

Again, at the foot of the tables 5-6 and 5-7 the means of the sample means (aluminium-capsule experiment, part I) and laboratory means (standard experiment) are given as well as the standard deviation and relative standard deviation of the single sample and of the single laboratory mean, respectively.

Comparison of the mean of the means gives no indication for the introduction of any significant systematic error for this sampling technique, neither. Comparison of the standard deviations shows that for this sampling technique, too, the spread of the values (which represents mainly the interlaboratory deviation) is certainly not significantly higher than for the standard experiment, although also in this case it has to be taken into consideration that the errors of aliquotation contribute additionally to the values calculated for the aluminium-capsule technique.

Tab. 5-5: IDA-72: Aluminium-Capsule Experiment I/Basic Data for Calculation of U-238 and Pu-239 Concentration (A-Sample Solution)

Column	1	2	3	4	5	6	7	8	9	10	11	12
					Uran				Plutonium			
Lab. Code	Sample	Capsule No.	Weight of mixed spike aliquot [g]	Weight of A-sample aliquot [g]	Ratio $\frac{\text{U-233}}{\text{U-238}}$ of unspiked A-solution[1]	Ratio $\frac{\text{U-238}}{\text{U-233}}$ of spike solution[1]	Number of MS run	Ratio $\frac{\text{U-233}}{\text{U-238}}$ of spiked A-solution	Ratio $\frac{\text{Pu-242}}{\text{Pu-239}}$ of unspiked A-solution[1]	Ratio $\frac{\text{Pu-239}}{\text{Pu-242}}$ of spike solution[1]	Number of MS run	Ratio $\frac{\text{Pu-242}}{\text{Pu-239}}$ of spiked A-solution
3	A-I	12	1.14548	1.14577	-	.0225	1	.6975	.0231	.0133	1	1.4483
							2	.6998			2	1.4452
							3	.6998			3	1.4474
	A-II	20	1.14107	1.15712	"	"	1	.6926	"	"	1	1.4269
							2	.6936			2	1.4247
							3	.6976			3	1.4243
6	A-I	11	1.13351	1.15805	-	.0221	1	.6940	.0231	.0133	1	1.393
							2	.6947			2	1.409
							3	.6957			3	1.408
	A-II	19	1.13665	1.17411	"	"	1	.6512	"	"	1	1.300
							2	.6527			2	1.302
							3	.6521			3	-[2]
13	A-I	13	1.14636	1.15951	-	.0221	1	.6983	.0226	.0133	1	1.4178
							2	.6987			2	1.4197
							3	.6986			3	1.4165
	A-II	21	1.13897	1.16267	"	"	1	.6965	"	"	1	1.4078
							2	.6954			2	1.4073
							3	.6956			3	1.4091
15	A-I	10	1.12825	1.14709	-	.0219	1	.6957	.0231	.0133	1	1.4080
							2	.6999			2	1.3969
							3	.6961			3	1.4048
	A-II	18	1.13158	1.17200	"	"	1	.6847	"	"	1	1.3818
							2	.6819			2	1.3876
							3	.6874			3	1.3821
17	A-I	15	1.14544	1.16000	-	.0223	1	.6992	.0228	.0133	1	1.4223
							2	.7002			2	1.4220
							3	.6997			3	1.4233
	A-II	23	1.14558	1.16904	"	"	1	.6943	"	"	1	1.4079
							2	.6949			2	1.4098
							3	.6961			3	1.4076
18	A-I	14	1.15133	1.17022	-	.0220	1	.7043	.0230	.0133	1	1.3988
							2	.7041			2	1.3962
							3	.7027			3	1.3975
	A-II	22	1.14528	1.16330	"	"	1	.7052	"	"	1	1.4090
							2	.7065			2	1.4113
							3	.7081			3	1.4056

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[1] Values taken from standard experiment /Vol. II, Par. 12.3/.

[2] Only two Pu-determinations on the A-II sample were reported.

Tab. 5-6: IDA-72 : Aluminium-Capsule Experiment I/U-238 Concentration Determination (A-Sample Solution)

Column	1	2	3	4	5	6	7	8	9
Lab. Code	Sample	Number of MS run	U-238 concentration [x10^{18} atoms/g sol.]	Mean concentration U-238 per sample [x10^{18} atoms/g sol.]	RSD of mean 1) [%]	Mean concentration U-238 per sample "calibrated" with sample R 2) [x10^{18} atoms/g sol.]	Lab. mean U-238 concentration standard exp. "calibrated" with sample R 2) [x10^{18} atoms/g sol.]	RSD of mean from stand. exp. 1) [%]	Deviation of mean value of Alu-capsule exp. from that of standard exp. [%]
3	A-I	1	2.953						
		2	2.943	2.947	.11	2.920			- .07
		3	2.943						
	A-II	1	2.934				2.922	.13	
		2	2.929	2.925	.22	2.898			- .82
		3	2.913						
6	A-I	1	2.907						
		2	2.904	2.903	.08	2.902			- .45
		3	2.899						
	A-II	1	(3.067) 3)				2.915	.28	
		2	(3.060) 3)	(3.063) 3)	.07	(3.062) 3)			+ 5.04
		3	(3.063) 3)						
13	A-I	1	2.918						
		2	2.916	2.917	.02	2.936			+ .86
		3	2.917						
	A-II	1	2.899				2.911	.03	
		2	2.904	2.902	.05	2.921			+ .34
		3	2.902						
15	A-I	1	2.914						
		2	2.896	2.908	.19	2.948			+ .65
		3	2.913						
	A-II	1	2.908				2.929	.32	
		2	2.919	2.908	.23	2.948			+ .65
		3	2.896						
17	A-I	1	2.910						
		2	2.906	2.908	.04	2.925			- 1.15
		3	2.908						
	A-II	1	2.909				2.959	.37	
		2	2.906	2.905	.08	2.922			- 1.25
		3	2.901						
18	A-I	1	2.879						
		2	2.879	2.881	.07	2.910			- .89
		3	2.885						
	A-II	1	2.877				2.936	.32	
		2	2.872	2.871	.12	2.900			- 1.23
		3	2.865						
				Mean of means		2.921)4)	2.929		
				SD		.018)4)	.017		
				RSD [%]		.61 4)	.59		

1) The relative standard deviations given in columns 5 and 8 are not directly comparable because of different layout of analytical steps.

2) For explanation and data see Par. 3.5.1 and Tab. 3-18.

3) Value considered as outlier.

4) Calculated without outlier value of sample II, lab. 6.

Tab. 5-7: IDA-72 : Aluminium-Capsule Experiment I/Pu-239 Concentration Determinations (A-Sample Solution)

Column	1	2	3	4	5	6	7	8	9
Lab. Code	Sample	Number of MS run	Pu-239 concentration $\left[x10^{16}\ \frac{atoms}{g\ sol.}\right]$	Mean concentration Pu-239 per sample $\left[x10^{16}\ \frac{atoms}{g\ sol.}\right]$	RSD of mean 1) [%]	Mean concentration Pu-239 per sample "calibrated" with sample R 2) $\left[x10^{16}\ \frac{atoms}{g\ sol.}\right]$	Lab. mean Pu-239 concentration standard exp. "calibrated" with sample R 2) $\left[x10^{16}\ \frac{atoms}{g\ sol.}\right]$	RSD of mean from stand. exp. 1) [%]	Deviation of mean value of dry spike exp. from that of standard exp. [%]
3	A-I	1	1.692	1.693	.06	1.705	1.713	.07	- .47
		2	1.696						
		3	1.693						
	A-II	1	1.695	1.697	.06	1.709			- .23
		2	1.697						
		3	1.698						
6	A-I	1	1.725	1.712	.37	-4)	-4)	.33	-4)
		2	1.704						
		3	1.706						
	A-II	1	1.832	(1.831) 3)	.08	-4)			-4)
		2	1.829						
		3	-5)						
13	A-I	1	1.710	1.709	.06	1.714	1.711	.01	+ .18
		2	1.707						
		3	1.711						
	A-II	1	1.707	1.706	.04	1.711			+ .0
		2	1.707						
		3	1.705						
15	A-I	1	1.714	1.720	.24	1.712	1.711	.24	- .06
		2	1.728						
		3	1.718						
	A-I	1	1.715	1.713	.14	1.705			- .35
		2	1.708						
		3	1.715						
17	A-I	1	1.702	1.702	.03	1.713	1.725	.14	- .70
		2	1.703						
		3	1.701						
	A-II	1	1.707	1.707	.05	1.718			- .41
		2	1.705						
		3	1.708						
18	A-I	1	1.726	1.727	.05	1.725	1.704	.04	+ 1.23
		2	1.729						
		3	1.728						
	A-II	1	1.714	1.714	.12	1.712			+ .47
		2	1.711						
		3	1.718						
				Mean of means		1.712	1.713		
				SD		.006	.008		
				RSD [%]		.35	.45		

1) The relative standard deviations given in columns 5 and 8 are not directly comparable because of different layout of analytical steps.

2) For explanation and data see Par. 3.5.1 and Tab. 3-19.

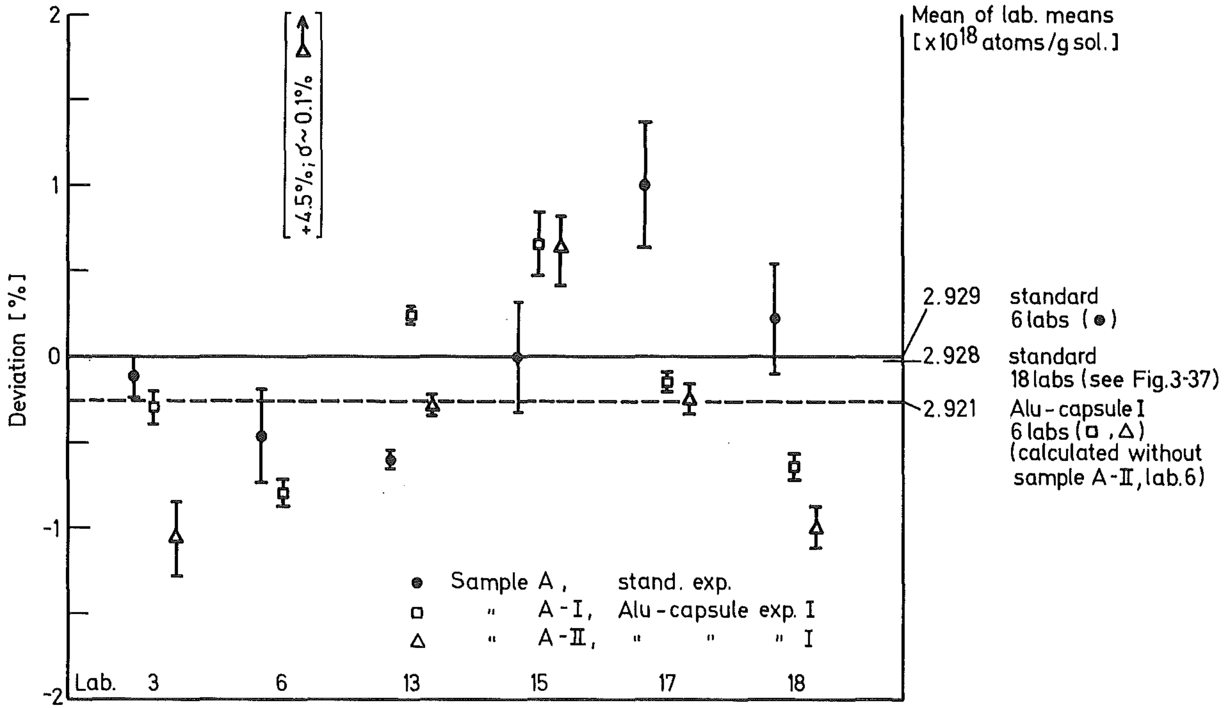
3) Value considered as outlier.

4) No meaningful values can be given, as the concentration value obtained in the standard experiment on the R-solution was an outlier.

5) Only two Pu-determinations on the A-II sample were reported.

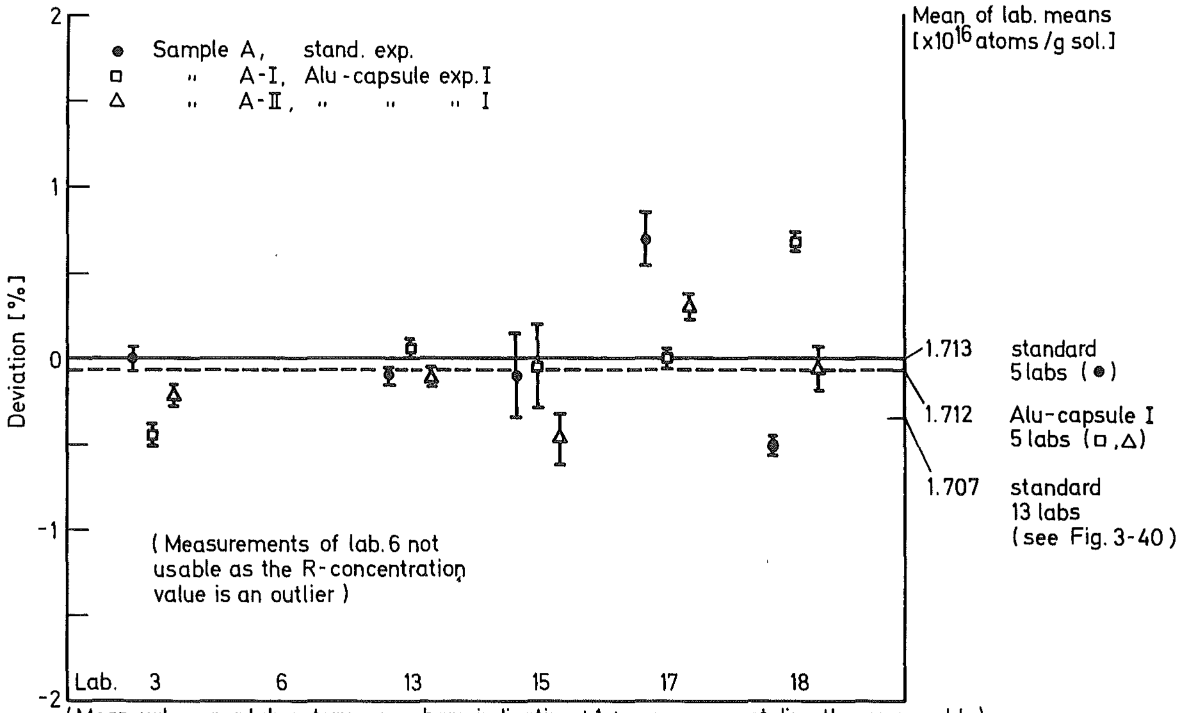
A graphical presentation of these results is given in Figures 5-4 and 5-5. The mean values calculated from the "calibrated" data obtained in the standard experiment by those laboratories which participated in this test were taken as reference values. Also the mean values for the "calibrated" A-sample calculated on the basis of the measurements of all participants in the standard experiment /Fig. 3-37 and 3-40/ are indicated.

The Pu-239/U-238 ratios calculated from the data obtained in this part of the aluminium-capsule experiment are compiled in Table 5-8 together with the corresponding values of the standard experiment. As observed in all former parts of the IDA-experiment /Par. 3.5.5, 4.2 and 5.1.2/, also these figures give no indication for a more accurate determination of these ratios than for the concentrations of the individual elements /Tab. 5-6 and 5-7/.



(Mean values per laboratory; error bars indicating ± 1σ-range are not directly comparable)

Fig.5-4 IDA-72 : Alu-Capsule Exp. I/U238-Concentration of Samples
A-I and A-II in Comparison with Sample A of Standard Experiment
(All Values "Calibrated" with Sample R)



(Mean values per laboratory, error bars indicating ± 1σ-range are not directly comparable)

Fig.5-5 IDA-72 : Alu-Capsule Exp. I / Pu 239-Concentration of Samples
A-I and A-II in Comparison with Sample A of Standard Experiment
(All Values "Calibrated" with Sample R)

Tab. 5-8: IDA-72: Aluminium-Capsule Experiment I
Pu-239/U-238 Concentration Ratios
(A-Sample Solution)

Column	1	2	3	4
Lab. Code	Sample	Atomic ratio $\frac{\text{Pu-239}}{\text{U -238}}$ from Alu-capsule exp. $[\times 10^{-2}]$	Atomic ratio $\frac{\text{Pu-239}}{\text{U -238}}$ from stand. exp. $[\times 10^{-2}]$	Deviation of lab. mean value of Alu-capsule exp. from that of stand. exp. [%]
3	A-I	.5839	.5862	- .39
	A-II	.5897		+ .60
6	A-I	-1)	-1)	-1)
	A-II			
13	A-I	.5838	.5878	- .68
	A-II	.5858		- .34
15	A-I	.5807	.5842	- .60
	A-II	.5784		- .99
17	A-I	.5856	.5830	+ .45
	A-II	.5880		+ .86
18	A-I	.5928	.5804	+2.14
	A-II	.5903		+1.71
Mean of means		.5859	.5843	
SD		.0044	.003	
RSD [%]		.76	.49	

All data calculated from "calibrated" values.

1) No meaningful "calibrated" Pu-239 concentration value available, as Pu-concentration determination on R-solution in the standard experiment was an outlier /Tab. 3-19/.

5.3 The Aluminium-Capsule Experiment Part II

5.3.1 Layout and Participation

Unlike the case of the dry spike technique, the complete dissolution of the loaded aluminium-capsules offers the possibility to transport exaxtly known quantities of sample material in the solid state /Par. 2.1/. In order to prove this quality of the aluminium-cpasule sampling technique, in part II of this test aliquots of the mixed spike solution and of the A-sample solution were evaporated to dryness in separate capsules. By dissolution of these capsules, the individual laboratories prepared spike- and sample solutions which were now used as starting material for the usual isotope dilution procedure. A scheme of this experimental layout is given in Fig. 5-6.

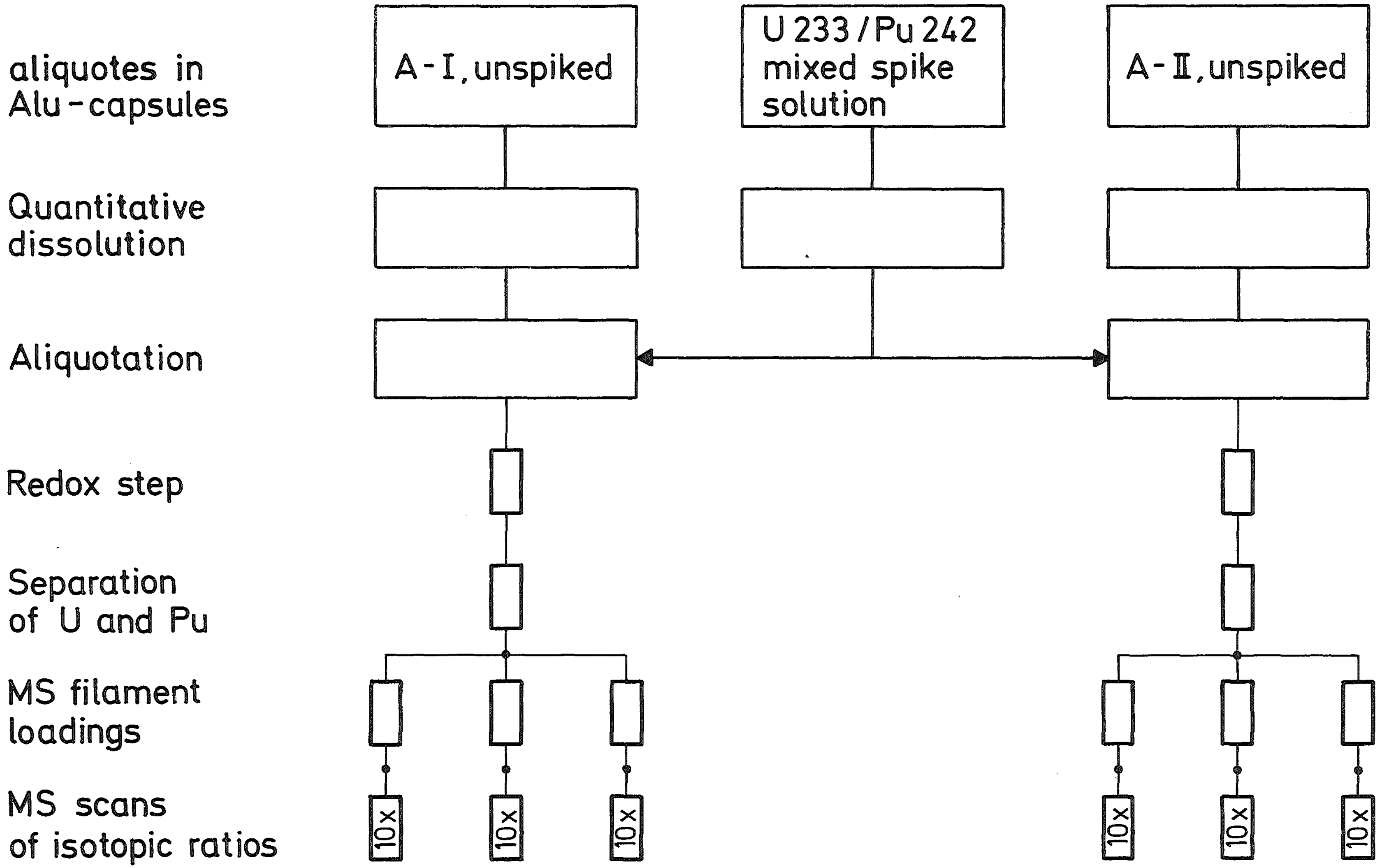
For each laboratory, two capsules with sample solution, marked "A-I" and "A-II", and one capsule with mixed spike solution were prepared at CBNM in collaboration with representatives of the Transuranium Institute /Vol. II, Par. 3.3.2 and Vol. II, Chapt. 5/. After dissolution, each of the two A-solutions was spiked once, passed the usual sample preparation steps and was then measured in three mass spectrometer runs (three filament loadings). The exact weights of the aliquots in the capsules were unknown to the laboratories at the time of analysis.

This test was performed by five of the laboratories which participated also in part I of these studies.

The following peculiarities were reported:

Lab. 3	used for the aliquotation the entire A-sample material obtained after dissolution,
Lab. 13	diluted Alu-capsule II only and made two aliquotations using the material of this same dilution.

Fig. 5-6: IDA-72 : Analytical Procedure of the Alu-Capsule II Experiment



(•) indicate branching points

5.3.2 Concentration Determinations

In Table 5-9 all data for calculating the concentrations of the spike solution are compiled. The individual laboratories obtained this spike solution by dissolution of the capsule loaded with mixed spike material.

The data for the capsules with A-sample material and their dissolution are given in Table 5-10. For each capsule a concentration factor F was calculated, defined by

$$F = \frac{\text{Total amount of A-sample solution obtained after dissolution of capsule } [g]}{\text{A-sample solution aliquot evaporated in capsule } [g]}$$

The three mass spectrometer run mean values of the isotopic ratios U-233/U-238 and Pu-241/Pu-239 obtained for the spiked samples are compiled in Tables 5-11 and 5-12 together with all data necessary for calculating the concentration. Finally, the calculated concentration values are summarized in Tables 5-13 and 5-14 for U-238 and Pu-239, respectively.

The comparison of the results with the data obtained by these laboratories in the standard experiment was again made on the basis of the "calibrated" concentration values for the reason discussed before /Par. 5.1.2/. The plutonium concentration determined by laboratory 15 on sample A-I was considered as outlier.

Also in this test the relative standard deviations calculated for the sample means of the aluminium-capsule technique (column 5) and for the laboratory means of the standard experiment (column 8) are not directly comparable. Those of the standard experiment also contain contributions from the chemical sample preparation steps in addition to the errors of the mass spectrometer measurement and, therefore, should be higher. However, this is not always the case.

At the foot of the Tables 5-13 and 5-14 again the means of the sample means (aluminium-capsule experiment) and the laboratory means (standard experiment) are given together with the standard deviation and relative standard deviation of the single sample and of the single laboratory mean, respectively. These standard deviations, which are mainly determined by the interlaboratory deviation, contain additional contributions of the aliquotation procedure performed by the individual laboratory in case of the aluminium-capsule technique according to the structure of this experiment /Fig. 5-6/ - unlike the conditions in the standard experiment. Taking into consideration this fact, the results are very satisfactory for both, uranium and plutonium.

A graphical presentation of these results is given in Figures 5-7 and 5-8 in the same manner as in part I of this test /Par.5.2.2/. As mentioned above, the plutonium determination on sample A-I by laboratory 15 was considered as outlier and not used for calculating the mean of the means.

In Table 5-15 the Pu-239/U-238 ratios calculated from the data obtained in this part of the aluminium capsule experiment are summarized together with the corresponding values from the standard experiment. There is no indication for a more accurate determination of these ratios than for the concentrations of the individual elements /Table 5-13 and 5-14/ in agreement with the results in all the other parts of the IDA-experiment.

Tab. 5-9: IDA-72: Aluminium-Capsule Experiment II/Calculation of Spike Solution Concentrations.

Column	1	2	3	4	5	6	7	8
Lab. Code	Capsule No.	Mixed spike solution aliquot [g]	Total amount of spike isotope in the capsule 1)		Total amount of spike solution after dissolution of capsule [g]	Concentration of spike solution obtained		Date of dissolution
			U-233 [$x10^{18}$ atoms]	Pu-242 [$x10^{16}$ atoms]		U-233 [$x10^{18}$ $\frac{\text{atoms}}{\text{g.sol.}}$]	Pu-242 [$x10^{16}$ $\frac{\text{atoms}}{\text{g sol.}}$]	
3	4	1.15465	2.4168	2.8397	34.0545	.07097	.08339	4.10.72
13	5	1.15741	2.4226	2.8465	19.5027	.12422	.14595	14.11.72
15	2	1.14926	2.4055	2.8265	22.91387	.10498	.12335	25.10.72
17	7	1.16143	2.4310	2.8564	19.56570	.12425	.14599	28.11.72
18	6	1.15182	2.4109	2.8328	64.55592	.03735	.04388	14. 9.72

1) Calculated on the basis of 2.0931 x 10^{18} atoms U-233/g sol. and 2.4594 x 10^{16} atoms Pu-242/g sol. (see pages 21 and 56)

Tab. 5-10: IDA-72: Aluminium-Capsule Experiment II/Calculation of Concentration Correction Factor "F" for Solutions of A-Sample Material.

Column	1	2	3	4	5	6
Lab. Code	Sample description	Capsule No.	A-Sample solution aliquot [g]	Total amount of A-sample solution after dissolution of capsule [g]	Concentration correction factor F[2]	Date of dissolution
3	A-I A-II	28 36	1.16342 1.17055	32.0763 29.4062	27.5707 25.1217	4.10.72 "
13	–[1] A-II	– 37	– 1.15449	– 17.5002	– 15.1584	– 14.11.72
15	A-I A-II	26 34	1.16148 1.14995	24.39860 22.45306	21.0065 19.5252	25.10.72 "
17	A-I A-II	31 39	1.15271 1.14770	18.05515 17.89380	15.6632 15.5910	28.11.72 "
18	A-I A-II	30 38	1.16379 1.13964	64.68132 64.65190	55.5782 56.7301	15. 9.72 "

[1] No values on the dilution of the capsule with sample "A-I" were reported.

[2] $$F = \frac{\text{Total amount of A-sample solution after dissolution of capsule } [g]}{\text{A-sample solution aliquot given into capsule } [g]}$$

Tab. 5-11: IDA-72 : Aluminium-Capsule Experiment II/Basic Data for Calculation of U-238 Concentrations (A-Sample Solution)

Column	1	2	3	4	5	6	7	8	9	10
Lab. Code	Sample	Date of aliquotation	Weight of mixed spike aliquot [g]	Weight of A-sample aliquot [g]	U-233 concentration of spike solution 1) [x10^{18} $\frac{\text{atoms}}{\text{g sol.}}$]	Concentration correction factor 2) F	Ratio $\frac{U-233}{U-238}$ of unspiked A-solution 3)	Ratio $\frac{U-238}{U-233}$ of spike solution 3)	Number of MS run	Ratio $\frac{U-233}{U-238}$ of spiked A-solution
3	A-I	4.10.72	13.8152	32.0763 4)	.07097	27.5707	-	.0225	1	.2841
									2	.2846
									3	.2859
	A-II	"	19.3583	29.4062 4)	"	25.1217	"	"	1	.3955
									2	.3960
									3	.3957
13 5)	A-II-1	15.11.72	3.8402	3.9909	.12422	15.1584	-	.0221	1	.6121
									2	.6116
									3	.6127
	A-II-2	"	3.8559	3.7437	"	15.1584	"	"	1	.6551
									2	.6542
									3	.6542
15	A-I	26.10.72	1.10340	1.09249	.10498	21.0065	-	.0219	1	.7560
									2	.7509
									3	.7516
	A-II	"	1.10351	1.19099	"	19.5252	"	"	1	.6474
									2	.6426
									3	.6425
17	A-I	29.11.72	3.81725	5.59485	.12425	15.6632	-	.0223	1	.4513
									2	.4523
									3	.4498
	A-II	"	4.03205	5.70720	"	15.5910	"	"	1	.4636
									2	.4616
									3	.4623
18	A-I	20. 9.72	.67100	1.29120	.03735	55.5782	-	.0220	1	.3714
									2	.3723
									3	.3714
	A-II	"	.66500	1.29660	"	56.7301	"	"	1	.3732
									2	.3729
									3	.3726

1) Values taken from Tab. 5-9, column 6.

2) Values taken from Tab. 5-10, column 5.

3) Values taken from standard experiment /Vol. II, Par. 12.3/.

4) Entire sample taken.

5) This laboratory diluted Alu-capsule II only and made two aliquotations using the material of this same dilution.

Tab. 5-12: IDA-72 : Aluminium-Capsule Experiment II/Basic Data for Calculation of Pu-239 Concentrations (A-Sample Solution)

Column	1	2	3	4	5	6	7	8	9	10
Lab. Code	Sample	Date of aliquotation	Weight of mixed spike aliquot [g]	Weight of A-sample aliquot [g]	Pu-242 concentration of spike solution 1) $\left[\times 10^{16} \frac{\text{atoms}}{\text{g sol.}}\right]$	Concentration correction factor 2) F	Ratio $\frac{\text{Pu-242}}{\text{Pu-239}}$ of unspiked A-solution 3)	Ratio $\frac{\text{Pu-239}}{\text{Pu-242}}$ of spike solution 3)	Number of MS run	Ratio $\frac{\text{Pu-242}}{\text{Pu-239}}$ of spiked A-solution
3	A-I	4.10.72	13.8152	32.0763 4)	.08339	27.5707	.0231	.0133	1	.6036
									2	.6010
									3	.6041
	A-II	"	19.3583	29.4062 4)	"	25.1217	"	"	1	.8276
									2	.8253
									3	.8285
13 5)	A-II-1	15.11.72	3.8402	3.9909	.14595	15.1584	.0226	.0133	1	1.242
									2	1.243
									3	-6)
	A-II-2	"	3.8559	3.7437	"	15.1584	"	"	1	1.330
									2	1.330
									3	1.332
15	A-I	26.10.72	1.20478	1.19132	.12335	21.0065	.0231	.0133	1	1.565
									2	1.573
									3	1.574
	A-II	"	1.10632	1.09591	"	19.5252	"	"	1	1.409
									2	1.425
									3	1.422
17	A-I	29.11.72	3.81725	5.59485	.14599	15.6632	.0228	.0133	1	.9334
									2	.9339
									3	.9342
	A-II	"	4.03205	5.70720	"	15.5910	"	"	1	.9522
									2	.9516
									3	.9547
18	A-I	19. 9.72	6.39230	12.61300	.04388	55.5782	.0230	.0133	1	.7313
									2	.7348
									3	.7334
	A-II	"	6.45790	12.70450	"	56.7301	"	"	1	.7505
									2	.7538
									3	.7534

1) Values taken from Tab. 5-9, column 7.

2) Values taken from Tab. 5-10, column 5.

3) The value determined by CBNM was used /Par. 3.5.1/.

4) Entire sample taken.

5) This laboratory diluted Alu-capsule II only and made two aliquotation using the material of this same dilution.

6) Only two determinations were reported for this sample.

Tab. 5-13: IDA-72 : Aluminium-Capsule Experiment II/U-238 Concentration Determinations (A-Sample Solution)

Column 1		2	3	4	5	6	7	8	9
Lab. Code	Sample	Number of MS run	U-238 concentration $[\times 10^{18}\ \frac{\text{atoms}}{\text{g sol.}}]$	Mean concentration U-238 per sample $[\times 10^{18}\ \frac{\text{atoms}}{\text{g sol.}}]$	RSD of mean 1) [%]	Mean concentration U-238 per sample "calibrated" with sample R 2) $[\times 10^{18}\ \frac{\text{atoms}}{\text{g sol.}}]$	Lab. mean U-238 concentration standard exp. "calibrated" with sample R 2) $[\times 10^{18}\ \frac{\text{atoms}}{\text{g sol.}}]$	RSD of mean from stand. exp. 1) [%]	Deviation of mean value of Alu-capsule exp. from that of standard exp. [%]
3	A-I	1	2.947						
		2	2.942	2.939	.18	2.912			- .34
		3	2.929						
	A-II	1	2.941				2.922	.13	
		2	2.937	2.939	.04	2.912			- .34
		3	2.940						
13 3)	A-II-1	1	2.920						
		2	2.922	2.920	.05	2.939			+ .96
		3	2.917						
	A-II-2	1	2.918				2.911	.03	
		2	2.922	2.921	.05	2.940			+ 1.00
		3	2.922						
15	A-I	1	2.897						
		2	2.917	2.910	.22	2.950			+ .72
		3	2.915						
	A-II	1	2.892				2.929	.32	
		2	2.914	2.907	.25	2.947			+ .61
		3	2.914						
17	A-I	1	2.913						
		2	2.906	2.914	.16	2.931			- .95
		3	2.922						
	A-II	1	2.922				2.959	.37	
		2	2.934	2.929	.12	2.946			- .44
		3	2.930						
18	A-I	1	2.881						
		2	2.874	2.879	.08	2.910			- .89
		3	2.881						
	A-II	1	2.888				2.936	.32	
		2	2.890	2.890	.05	2.921			- .51
		3	2.893						
				Mean of means		2.931	2.931		
				SD		.016	.018		
				RSD [%]		.54	.61		

1) The relative standard deviations given in columns 5 and 8 are not directly comparable because of different layout of analytical steps.

2) For explanation and data see Par. 3.5.1 and Tab. 3-18.

3) This laboratory diluted Alu-capsule II only made two aliquotations using the material of this same dilution.

Tab. 5-14: IDA-72 : Aluminium-Capsule Experiment II/Pu-239 Concentration Determinations (A-Sample Solution)

Column	1	2	3	4	5	6	7	8	9
Lab. Code	Sample	Number of MS run	Pu-239 concentration $\left[x10^{16} \frac{atoms}{g\ sol.}\right]$	Mean concentration Pu-239 per sample $\left[x10^{16} \frac{atoms}{g\ sol.}\right]$	RSD of mean[1] [%]	Mean concentration Pu-239 per sample "calibrated" with sample R[2] $\left[x10^{16} \frac{atoms}{g\ sol.}\right]$	Lab.mean Pu-239 concentration standard exp. "calibrated" with sample R[2] $\left[x10^{16} \frac{atoms}{g\ sol.}\right]$	RSD of mean from stand. exp. [1] [%]	Deviation of mean value of Alu-capsule exp. from that of standard exp. [%]
3	A-I	1	1.692	1.694	.17	1.706	1.713	.07	- .41
		2	1.700						
		3	1.691						
	A-II	1	1.695	1.696	.12	1.708			- .29
		2	1.700						
		3	1.693						
13[3]	A-I-1	1	1.718	1.717	.06	1.722	1.711	.01	+ .64
		2	1.716						
		3	-4)						
	A-II-2	1	1.713	1.712	.06	1.717			+ .35
		2	1.713						
		3	1.710						
15	A-I	1	1.664	(1.658) 5)	.19	(1.650) 5)	1.711	.24	- .57
		2	1.655						
		3	1.654						
	A-II	1	1.721	1.709	.36	1.~~6~~701			- .58
		2	1.701						
		3	1.705						
17	A-I	1	1.692	1.691	.02	1.701	1.725	.14	-1.39
		2	1.691						
		3	1.691						
	A-II	1	1.708	1.707	.09	1.718			- .41
		2	1.709						
		3	1.704						
18	A-I	1	1.728	1.723	.15	1.721	1.704	.04	+1.00
		2	1.719						
		3	1.723						
	A-II	1	1.720	1.715	.15	1.713			+ .53
		2	1.712						
		3	1.713						
				Mean of means		1.712	1.713		
				SD		.008	.00 8		
				RSD [%]		.48	.45		

---

[1] The relative standard deviations given in columns 5 and 8 are not directly comparable because of different layout of analytical steps.

[2] For explanation and data see Par. 3.5.1 and Tab. 3-19.

[3] This laboratory diluted Alu-capsule II only and made two aliquotations using the material of this same dilution.

[4] Only two determinations were reported for this sample.

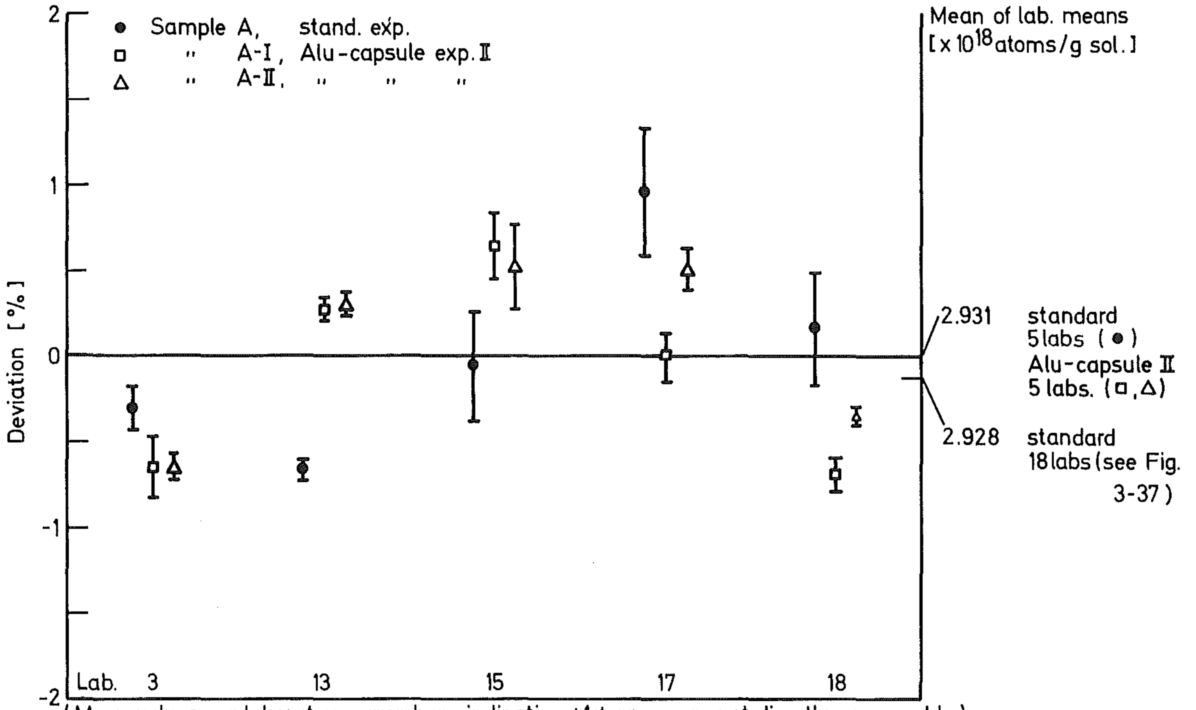
[5] Value considered as outlier and not used for calculation of mean of means.

Tab. 5-15: IDA-72: **Aluminium-Capsule Experiment II**
Pu-239/U-238 Concentration Ratios
(A-Sample Solution)

Column	1	2	3	4
Lab. Code	Sample	Atomic ratio $\frac{\text{Pu-239}}{\text{U -238}}$ from Alu-capsule exp. $[\times 10^{-2}]$	Atomic ratio $\frac{\text{Pu-239}}{\text{U -238}}$ from standard exp. $[\times 10^{-2}]$	Deviation of lab. mean value of Alu-capsule exp. from that of standard exp. [%]
3	A-I A-II	.5859 .5865	.5862	- .05 + .05
13	A-I A-II	.5859 .5840	.5878	- .32 - .65
15	A-I A-II	(.5593)[1)] .5772	.5842	- 4.26 - 2.40
17	A-I A-II	.5803 .5832	.5830	- .46 + .03
18	A-I A-II	.5914 .5864	.5804	+ 1.90 + 1.03
Mean of means		.5845	.5843	
SD		.0041	.0029	
RSD [%]		.69	.49	

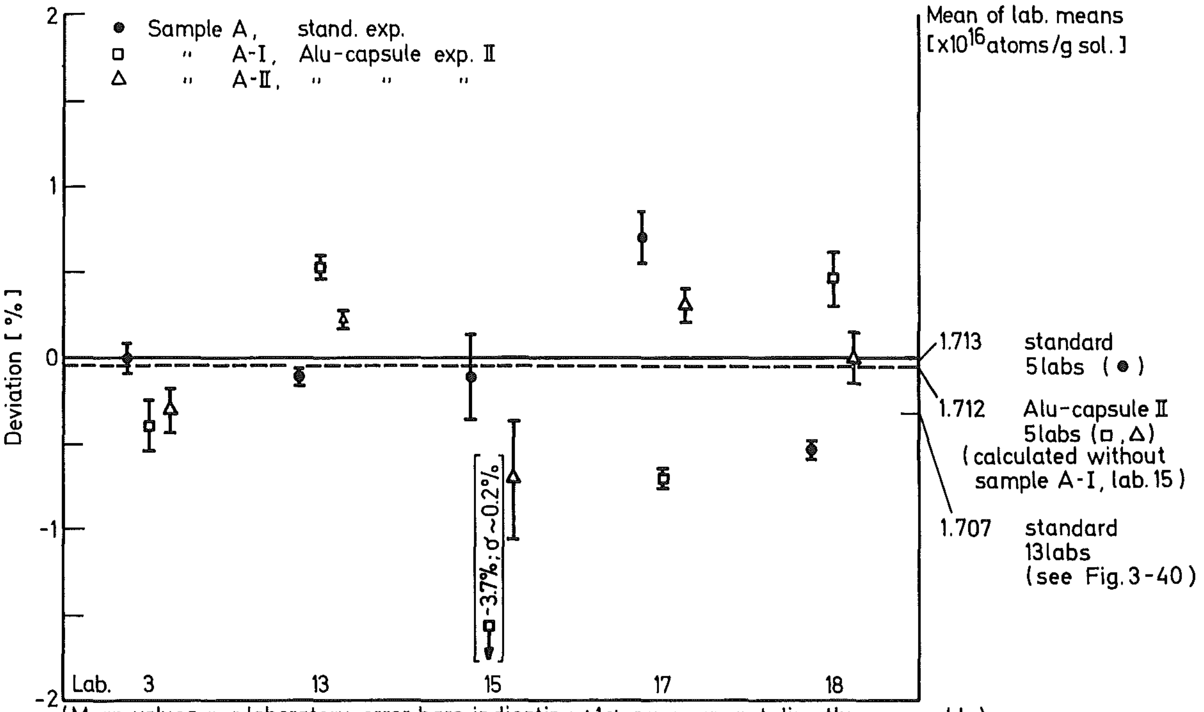
All data calculated from "calibrated" values.

[1)] Plutonium determination was considered as outlier.



(Mean values per laboratory; error bars indicating ±1σ-range are not directly comparable)

Fig.5-7 IDA-72 : Alu-Capsule Exp.II / U238-Concentration of Samples A-I and A-II in Comparison with Sample A of Standard Experiment (All Values "Calibrated" with Sample R)



(Mean values per laboratory; error bars indicating ±1σ-range are not directly comparable)

Fig.5-8 IDA-72: Alu-Capsule Exp.II / Pu239-Concentration of Samples A-I and A-II in Comparison with Sample A of Standard Experiment (All Values "Calibrated" with Sample R)

5.4 Compilation of Results

The main results of testing the new techniques of sample conditioning described in this chapter are compiled in Table 5-16 and compared to the data obtained by the use of liquid sample material in the standard experiment.

The small deviations of the mean values from those obtained in the standard experiment (columns 1 and 2) confirm that no significant systematic error is introduced by the new techniques.

Furthermore, the similar values for the relative standard deviations of the laboratory means (compared to those obtained in the standard experiment; columns 3 and 4) indicate clearly that there is also no increase in the spread of the results although the tests of the new techniques contained more individual analytical steps than the standard experiment.

Tab. 5-16: IDA-72: Results of Dry Spike and Aluminium-Capsule Experiments in Comparison to the Standard Experiment

Column	1	2	3	4	5	6	
Experiment	Deviation of mean of lab. means from mean of lab. means of standard experiment %		RSD of lab. means [%]		Number of labs which participated in the experiment	Number of labs and samples on which calculation was based:	
	U	Pu	U	Pu		U	Pu
Dry spike Standard 1)	+ 0.21	± 0.0	0.43 0.57	0.30 0.43	8	7/14 2)	6/12 3)
Alu-capsule I Standard 1)	- 0.27	- 0.06	0.61 0.59	0.35 0.45	6	6/11 4)	5/10 5)
Alu-capsule II Standard 1)	± 0.0	- 0.06	0.54 0.61	0.48 0.45	5	5/10	5/9 4)

(A-solution, calculated from calibrated values)

1) Calculated from the same group of laboratories which participated in the corresponding experiment.

2) Values of one laboratory were excluded from this calculation, because they are probably outliers.

3) Measurements of two laboratories could not be used because the concentration value of the R-solution in the standard experiment was an outlier.

4) One determination considered as outlier.

5) One determination considered as outlier. Furthermore, the concentration value of the R-solution of the same laboratory in the standard experiment is an outlier.

6. The Aging Experiments

6.1 General Survey

It was the objective of these experiments to study the aging effects in diluted active feed solutions of reprocessing plants.

The dependence of these effects on

- the molarity of the nitric acid

- the concentration of plutonium

- the presence of fission products

- the time

should be investigated /Par. 2-1/.

The experiment was split into three parts. Part I was performed by the Joint Research Center of EURATOM in Ispra (Varese), Italy. In this part active solutions of three different molarities : 2.5 M, 5 M, and 8 M were studied, the time interval was 173 days.

Details are given in paragraph 6.2.

Part II of the aging experiment was executed at the Institut for Atomenergie in Kjeller, Norway. In this part active solutions with three different Pu concentrations : 2,10 and 20 µg Pu/ml were analysed, the time interval was 4.5 months (~135 days).

The report on these studies is given in par. 6.3 /*/.

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[*] It was written by M. Bonnevie-Svendsen, Kjeller

Part III is concerned with a comparison of the aging behavior of active and inactive solutions (similar to the active ones) in the short time range (2-10 days) and in the long time range (225 days). These measurements were performed in the Los Alamos Scientific Laboratory.
The report is included here as Par. 6.4.

The preparation of the samples is described in Vol. II, Par. 3.3.4 - 3.3.8. Reference is also made to Par. 2.2 of this volume.

The actual experiments were performed on those types of solutions which were analysed in other parts of the IDA-72 experiment also. Molarity and Pu concentration were extended to some contiguous values.

In the contect of the results of these studies the problems of aging effects and their investigation were thoroughly discussed by the experts at the final meeting /Par. 8.3.8/.

Overall one must say that the IDA-72 attempt to find and understand aging effects was not very sucessful due to lack of data. But in order to obtain meaningful data in general would mean a tremendous analytical effort, much larger then that invested in course of the IDA-72 experment.

6.2 Aging Experiment I

6.2.1 Objective

It was the objective of this experiment to study the dependence of aging effects in diluted active feed solutions on the molarity of the nitric acid over a time interval of some months.

6.2.2 Layout and Sample Preparation

In addition to the samples "A" and "B" used for the standard experiment, a third sample "C" was taken from the input tank at the EUROCHEMIC plant in the same sampling procedure /Par. 2.2 and Vol. II, Chapt. 2/. After storage for about 24 hours the sample was diluted with 5 $\underline{M}$ HNO_3 in a ratio of about 1:100. About 30 ml of this solution with a plutonium concentration of ~ 20 μg/ml (solution "D"/Fig. 2-2/) was subdivided into three parts which were further diluted with nitric acid of different molarity to obtain finally three sample solutions with a molarity of about 2.5, 5 and 8 $\underline{M}$, respectively, and a plutonium concentration in the order of 10 μg/ml. At the same day (immediately after these dilution steps), aliquots were taken from each of the three sample solutions and spiked by the CBNM with the same U-233/Pu-242 mixed spike solution as used in the standard experiment /Vol. II, Par. 3.3.7/. These samples which should be used to determine the initial concentrations were stabilized by addition of hydroxylamine and heating to 80° C for about one hour.

The residual unspiked sample material was filled into glass vials (two vials per sample type) and shipped to the laboratory of the C.C.R. Ispra together with the spiked samples and three vials with mixed spike solution.

Besides the determination of the initial concentration on the samples spiked at CBNM the laboratory performed one U[1] and Pu-concentration determination in duplicate (2 aliquotations) after a storage time of about 4 and 5,5 months on the sample solutions in each of the 6 vials, using the mixed spike solution supplied by CBNM. For the uranium analyses, quantitative dilutions were performed separately on sample and spike solution before aliquotation.

For valency adjustment, the plutonium of the spiked sample solution was reduced by hydroxylamine hydrochloride at 80°C for 10 min. and then oxidized by sodium nitrite.

6.2.3 Results

The mean values for the initial U-238 and Pu-239 concentrations obtained on the samples spiked at CBNM before shipment to the C.C.R. Ispra are summarized in Table 6-1 together with the calculated Pu-239/U-238 ratios. These data were "calibrated" with the concentration value obtained by this laboratory on sample R in the standard experiment /Par. 3.5.1/.

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1) For the U concentration determination after 4 months, the solution of only one vial was used for each molarity.

The relative changes in the uranium and plutonium concentrations after storage of the (diluted) sample material for about 4 months and 5.5 months, respectively, are shown graphically in Fig. 6-1 to 6-3. Each measuring point is calculated from the mean value of one mass spectrometer run. Three of the concentration determinations deviate considerably from all the other values. It seems problematic to decide whether or not these values are really caused by aging of the sample material or by other effects.

In case of the 2.5 M sample solution in vial 272, second aliquotation after 125 days (see Fig. 6-1), the high Pu concentration value found is confirmed neither by the value of the first aliquotation at the same time, nor by the analyses performed after 166 days.

In principle, it cannot be excluded that the high Pu concentration found in one single determination is caused by sampling of a polymerized particle which would indicate such an aging effect. However, it seems more likely that this outlier value is of the same kind as those observed in the standard experiment Fig. 3-38, where aging effects were excluded by immediately spiking the samples.

In case of the 8 M sample solution in vial 279, second aliquotation after 173 days (see Fig. 6-3), the extraordinary low concentration values are found for both, uranium and plutonium. As the aliquotations for uranium and plutonium were performed separately (see above, Par. 6.2.2) this indicates that the total concentration of the sample solution in this vial changed between the first and the second aliquotation.

Tab. 6-1: Initial U-238 and Pu-239 Concentrations and Resulting Pu-239/U-238 Concentration Ratios of the Sample Solution.

Vial No.	Molarity of samples	U-238 concentration*) $\left[\times 10^{18}\ \frac{\text{atoms}}{\text{g sol.}}\right]$	Pu-239 concentration*) $\left[\times 10^{16}\ \frac{\text{atoms}}{\text{g sol.}}\right]$	Atomic ratio $\frac{\text{Pu-239}}{\text{U-238}}$	Deviation from the Pu-239/U-238 ratio for the 5 M solution [%]
143	2.5 M	2.638	1.587	.6016	0.87
144	5 M	2.456	1.465	.5964	-
145	8 M	2.319	1.371	.5913	- 0.80
		-	Mean:	.5964	

*) Values given are those obtained after calibration with sample R /Par. 3.5.1/.

The concentration values deviate not more than 20% (at maximum) from those of the samples in the standard experiment. This confirms that the preparation of these samples resulted in the desired order of magnitude with respect to the Pu concentration. Theoretically, the Pu-239/U-238 ratios should be the same as the value obtained by this laboratory in the standard experiment on the A and B samples. However, the calculated mean value of 0.5964 is about 2.4 % higher. This is remarkable, as in the standard experiment the difference of those ratios between sample A and B does not exceed 1 % for any laboratory / Tab. 3-21 /. As inhomogenity of the tank solution seems to be very improbable /Vol. II, Par. 2.3.1/, aging during the storage of the undiluted sample material for about 24 hours (see above, Par. 6.2.2) may be the reason for this effect. However, the positive sign of the deviation excludes any explanation due to effects which lead to a loss of plutonium as e.g. plating out of plutonium on the walls of the vial.

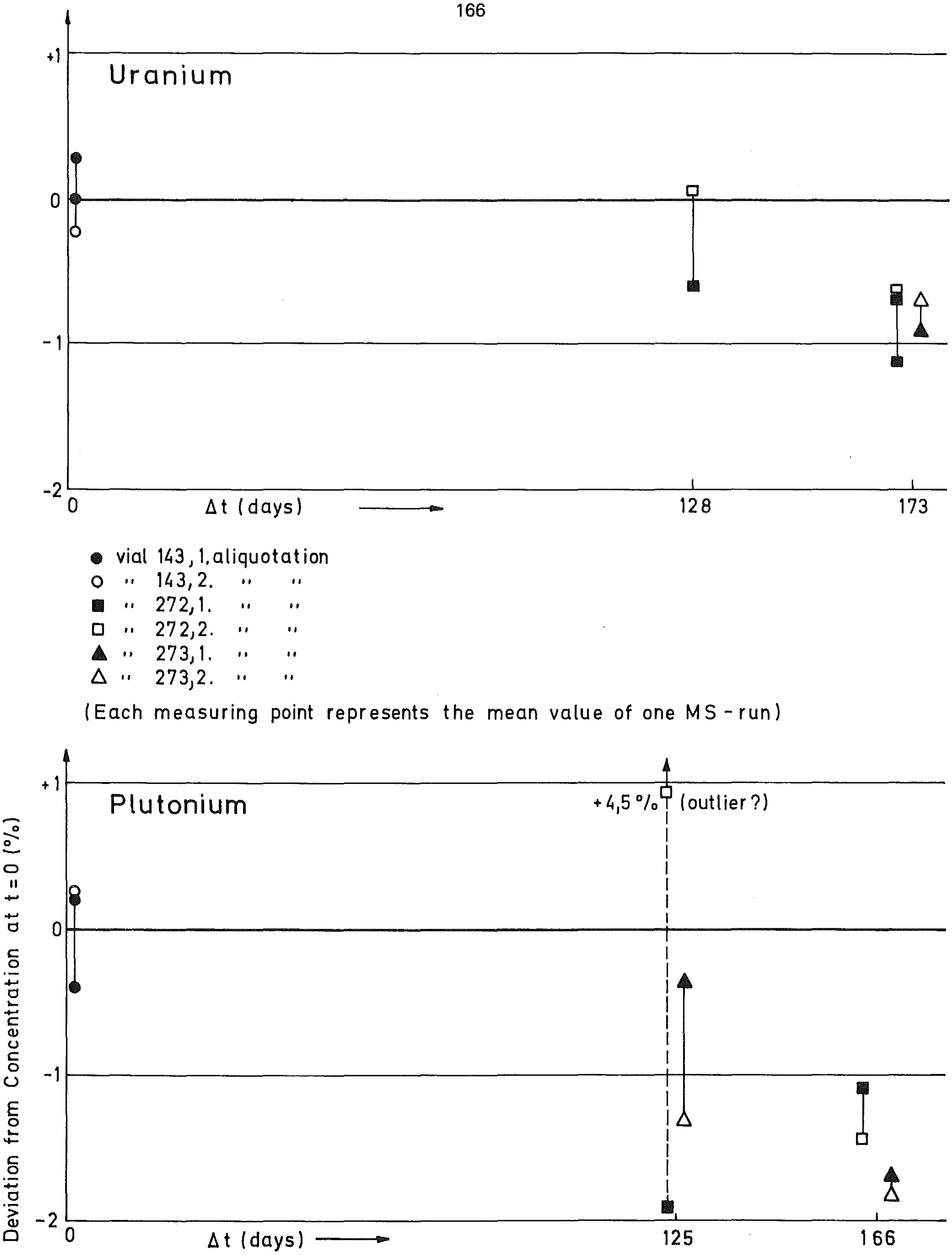

Fig.6-1 IDA-72 : Aging Experiment I / 2.5 M-Sample Concentrations.

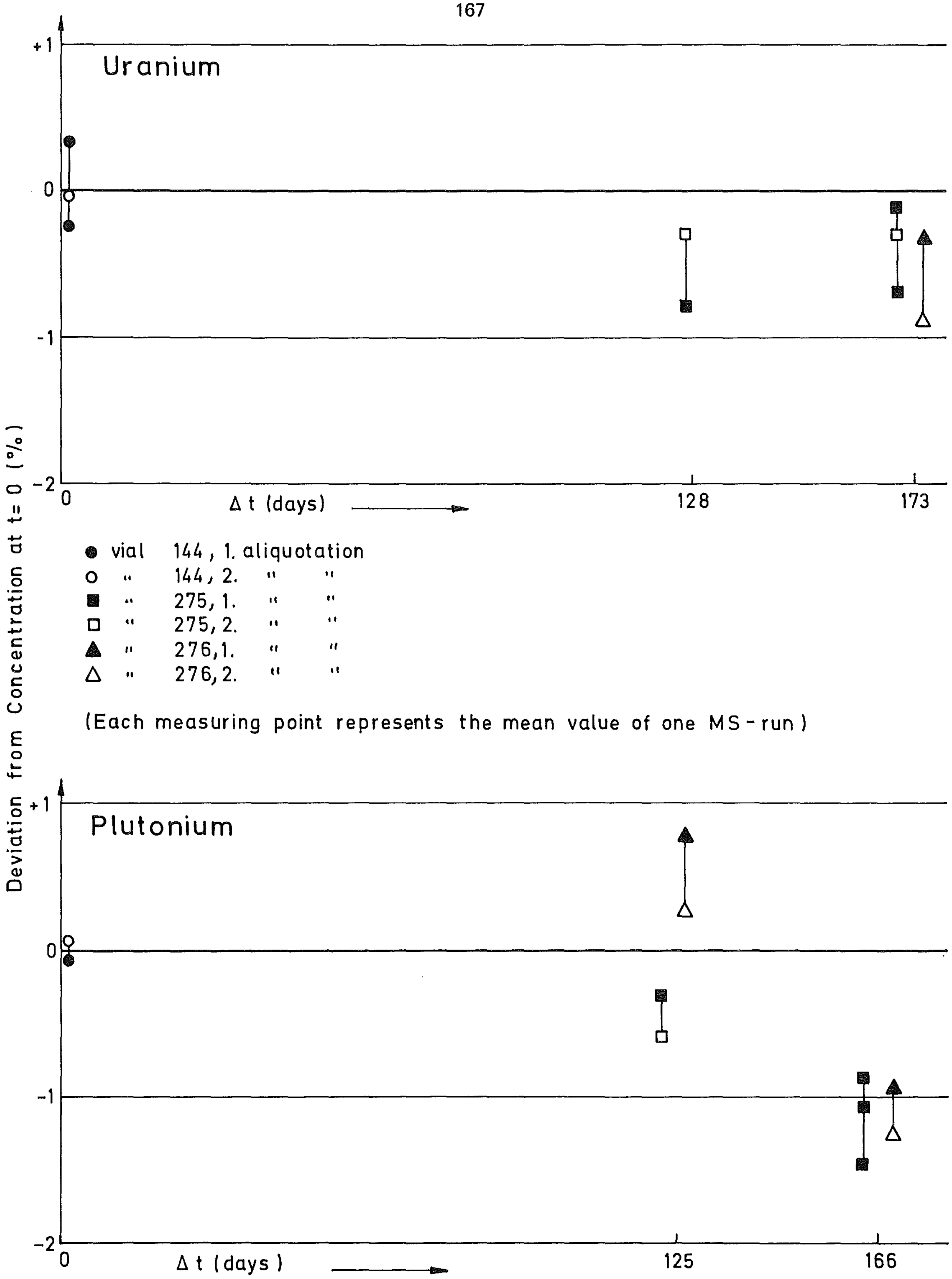

Fig.6-2 IDA-72 : Aging Experiment I/ 5 M-Sample Concentrations.

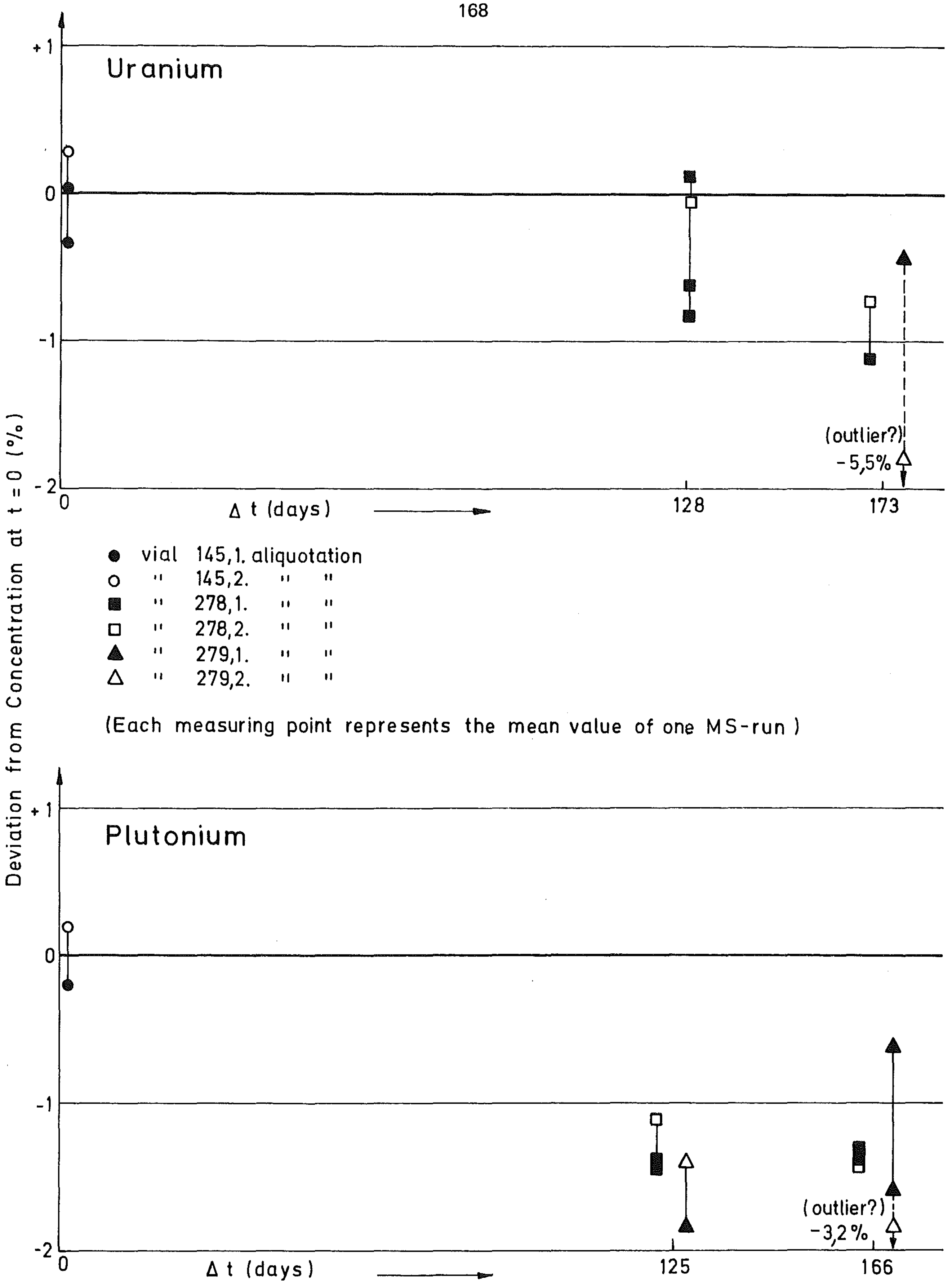

Fig.6-3 IDA-72: Aging Experiment I/8 M - Sample Concentrations.

If the three "outlier"values defined by these considerations remain disregarded, the results of this experiment can be summarized as follows:

1.) There is no indication for any concentration increase, e.g. by evaporation of sample solution.

2.) A concentration decrease up to 1 % for uranium and up to 2 % for plutonium is indicated.

3.) No significant difference can be observed in the behaviour of the sample solutions with the different molarities investigated.

6.3 Aging Experiment II

(by M. Bonnevie-Svendsen, Institutt for Atomenergi (IFA), Kjeller,Norway)

6.3.1 Objective

It was intended to study the influence of the plutonium concentration on aging effects in radioactive feed solutions.

6.3.2 Measurements

3 series of samples containing 2, 10 and 20 µg Pu/ml, resp., were studied. The nitric acid concentration was 5 M in all samples. An aliquot of each sample was spiked and subsequently conditioned by hydroxylamine treatment in Mol medio June (zero-spikes).[1] 3 further spikings were carried out at Kjeller after approx. $2\frac{1}{2}$, $3\frac{1}{2}$ and $4\frac{1}{2}$ months, see Fig. 6-4. To study possible "bottle effects" two samples of each series were assayed in parallel, U-233/Pu-242 mixed spike solutions were used for all spikings. Chemical separations preceeded by redox treatment with ferrous-ammonium-sulfate-$NaNO_2$ (GEAP 5354) were performed medio November 1972 and medio January 1973.

As additional experiments isotopic ratios in several extraction chromatographic Pu-fractions and in extracts from empty sample bottles were measured, and some control measurements on the spike solutions were carried out.

6.3.3 Results

For plutonium quite inconsistent results were obtained. There were great unsystematic variations within the experimental series and even between simultaneously spiked duplo samples and between parallels from the zero-spiked samples. No correlation with the time of spiking or with the plutonium concentration was observed.

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[1] For the preparation of these samples see Par. 2.2, Vol. II, Chapt. 2 and Vol. II, Par. 3.38.

Corresponding inconsistencies were not found for uranium. A certain unsystematic spread may be ascribed to malfunctions of the mass spectrometer*). Relative Pu and U concentrations are shown in Tables 6-2 and 6-3.

The main "aging effects" seem to have occured during the period elapsed between spiking and redox treatment. There are marked differences between parallel samples measured in November 1972 and in January 1973. The apparent increase in the Pu concentration with time seems to be caused by a reduction of the Pu-242 content in the samples. The effect is the same for samples spiked in Mol (zero-spiked) and at Kjeller. No such effects are observed for U.

The puzzling Pu results are possibly caused by the fact that small original sources of error have been strongly enhanced for aged samples. The effects could probably have been avoided if:

- the samples had been properly conditioned in connection with the spiking procedure,
- a more rigorous redox treatment had been applied prior to the chemical separation.

Thus the observed variations can hardly be defined as real aging effects, and not much seems to be gained by a quantitative evaluation of the data. Together with the extraction chromatographic studies the results may, however, be illustrative for the behaviour of plutonium in aged feed solutions.

6.3.4 Additional Experiment

Using an extraction chromatographic procedure /Ref. 5/ with TBP supported on hydrophobized Kieselguhr as the stationary phase, Pu was eluted in 3 fractions:

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*) During this period the mass spectrometer was badly in need for service. The ion current was unstable (standard dev. for the scans 0.5 - nearly 3%)

1. Pu III and other TBP-inextractable Pu species
2. Pu VI and other moderately extractable Pu species
3. Pu IV.

The first fraction was separated from other actiniedes and fission products by repeated extraction chromatography after oxidation to Pu IV.

Mass spectrometric isotope analyses of some Pu fractions are shown in Table 6-4.

- The ratio of Pu eluted in the two first fractions *) varies with the sample type. We find more Pu III in the samples, more Pu VI in the spike solutions.

- There are remarkable differences in the isotopic composition of different Pu fractions from the same sample. The highest 242/239 ratios are found in the Pu VI fractions.

- "Bottle effects" - i.e. isotopic fractionation on the walls of the sample bottles - appear to be insignificant for the original sample bottles, but a fractionation was observed in the extract from a secondary 2 ml sample flask used for storage of IFA-spiked samples.

- Repeated mass spectrometric analyses verified the high Pu-239 content in the U-233/Pu-242 mixed spike solutions.

- Both in the Pu III and Pu IV fractions from the mixed spike solutions the 242/239 ratios were low. In the Pu VI fractions the ratio was nearer to the specifications. This is further illustrated by the mass spectrometic scans in Fig. 6-5 and 6-6.

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*) We estimated that the amount of Pu in these two fractions varied between ~1 and 20%, but due to the simultaneous variation in isotopic composition quantitative results were not obtained.

6.3.5. Discussion

The experiments reveal a marked difference in the chemical state of plutonium in spike and sample solutions. This seems to impede the establishment of an isotopic equilibrium in the spiked samples. The hydroxylamine treatment has apparently not been efficient.

"Aging" during storage of the spiked samples appear to stabilize the "Pu VI - fraction", rendering even the ferrous-ammonium-sulfate treatment (GEAP 5354) inefficient. This would explain the decreasing Pu-242 content (accumulated in the Pu VI fraction) in aged samples and also the increasing spread in the analytical results.

The low 242/239 ratio in the mixed spike ($\sim$60 compared to nearly 5000 on the Pu-242 spike) could either be explained by a laboratory contamination or by a certain Pu-239 concentration in the U-233 spike. It is difficult to imagine how such a contamination could occur in all 3 spike vials. We would consider it more likely that some Pu-239 is contained in the U-233 spike. The mass spectrometric scan of Pu separated from the last rest of our U-233 spike solution (shown in Fig. 6-7) seems to verify this assumption.

Table 6-2 **IDA-72**

Relative Uranium Concentrations

Given as: $\frac{C - B}{A - C} \cdot 100 \cdot \frac{\text{weight spike}}{\text{weight sample}}$

where A = isotopic ratio 238/233 in unspiked sample

B = isotopic ratio 238/233 in spike

C = isotopic ratio 238/233 in spiked sample

Date of spiking / Date of chem.sep.	2 µg/Pu/ml		10 µg/Pu/ml		20 µg Pu/ml	
	15-17/11-72	16-19/1-73	15-17/11-72	16-19/1-73	15-17/11-72	16-19/1-73
t_o	Cs-2 1) 0.566	Cs-2 1) 0.559	Cs-10 2) 2.81	Cs-10 2) 2.71	Cs-20 3) 5.34	Cs-30 3) 5.38
6.9.72	13 a 4) 0.559	13 b 0.536	15 a 2.76	15 b 2.80	17 a 5.64	17 b 5.45
6.10.72		7 a 0.556		9 a		11 a 5.52
7.11.72	2 a 0.543	2 b 0.556	4 a 2.78	4 b 2.74	6 a 5.45	6 b 5.39
7.11.72	1 a 0.574	1 b -	3 a 2.86	3 b 2.77	5 a 5.59	5 b 5.49

1) Assumed ratio $\frac{\text{weight spike}}{\text{weight sample}} = 0.2151$

2) Assumed ratio $\frac{\text{weight spike}}{\text{weight sample}} = 1.192$

3) Assumed ratio $\frac{\text{weight spike}}{\text{weight sample}} = 2.028$

4) The bottle numbers refer to the numbers given in fig.6-4;a and b refer to the dates of chemical separation.

Table 6-3 IDA-72

Relative Plutonium Concentration

Given as: $\frac{C - B}{A - C} \cdot 100 \cdot \frac{\text{weight spike}}{\text{weight sample}}$

where A = isotopic ratio 239/242 in unspiked sample
B = isotopic ratio 239/242 in spike
C = isotopic ratio 239/242 in spiked sample

Date of spiking \ Date of chem. sep.	2 µg Pu/ml				10 µg Pu/ml				20 µg Pu/ml			
	15-17/11-72		16-19/1-73		15-17/11-72		16-19/1-73		15-17/11-72		16-19/1-73	
t_o	Cs-2 1)	0.300	Cs-2 1)	0.430	Cs-10 2)	2.44	Cs-10 2)	3.44	Cs-20 3)	2.70	Cs-20 3)	4.53
6.9.72	13 a 4)	0.277	13 b	0.384	15 a	2.33	15 b	3.55	17 a	2.56	17 b	3.44
6.10.72			7 a	0.286			9 a	2.36			11 a	3.11
7.11.72	2 a	0.278	2 b	0.438	4 a	2.77	4 b	2.30	6 a	3.15	6 b	3.27
7.11.72	1 a	0.274	1 b	-	3 a	3.03	3 b	2.32	5 a	3.95	5 b	3.00

1) Assumed ratio $\frac{\text{weight spike}}{\text{weight sample}} = 0.2151$

2) Assumed ratio $\frac{\text{weight spike}}{\text{weight sample}} = 1.192$

3) Assumed ratio $\frac{\text{weight spike}}{\text{weight sample}} = 2.028$

4) The bottle numbers refer to the numbers given in fig.6-4;a and b refer to the dates of chemical separation.

Table 6-4 IDA-72

Isotopic ratios measured in different Pu-fractions

Sample type	MIXED SPIKE				SPIKED SAMPLES				UNSPIKED SAMPLE
					Mol. zero spike 22.6.72		IFA first spike 6.9.73		
Sample No.	Vial 109 1)		Vial 107		Cs-20		18 b	17 a	Cu-5
Isotopes	242/239	240/239	242/239	240/239	242/239		242/239		242/239
Bulk Pu	69.7	0.447	65.1 1)	0,430 1)	1.674	0,964 2)	-	0.856	0.023
Bottle extract.	-	-	56.4	0.421	1.673		0.243 3)	-	-
Pu III	-	-	10.8 4)	0.335	2.50		0.060	-	-
Pu VI	-	-	1993	2.13	128		1.280	-	-
Pu IV	-	-	14.9	0.406	0.136				

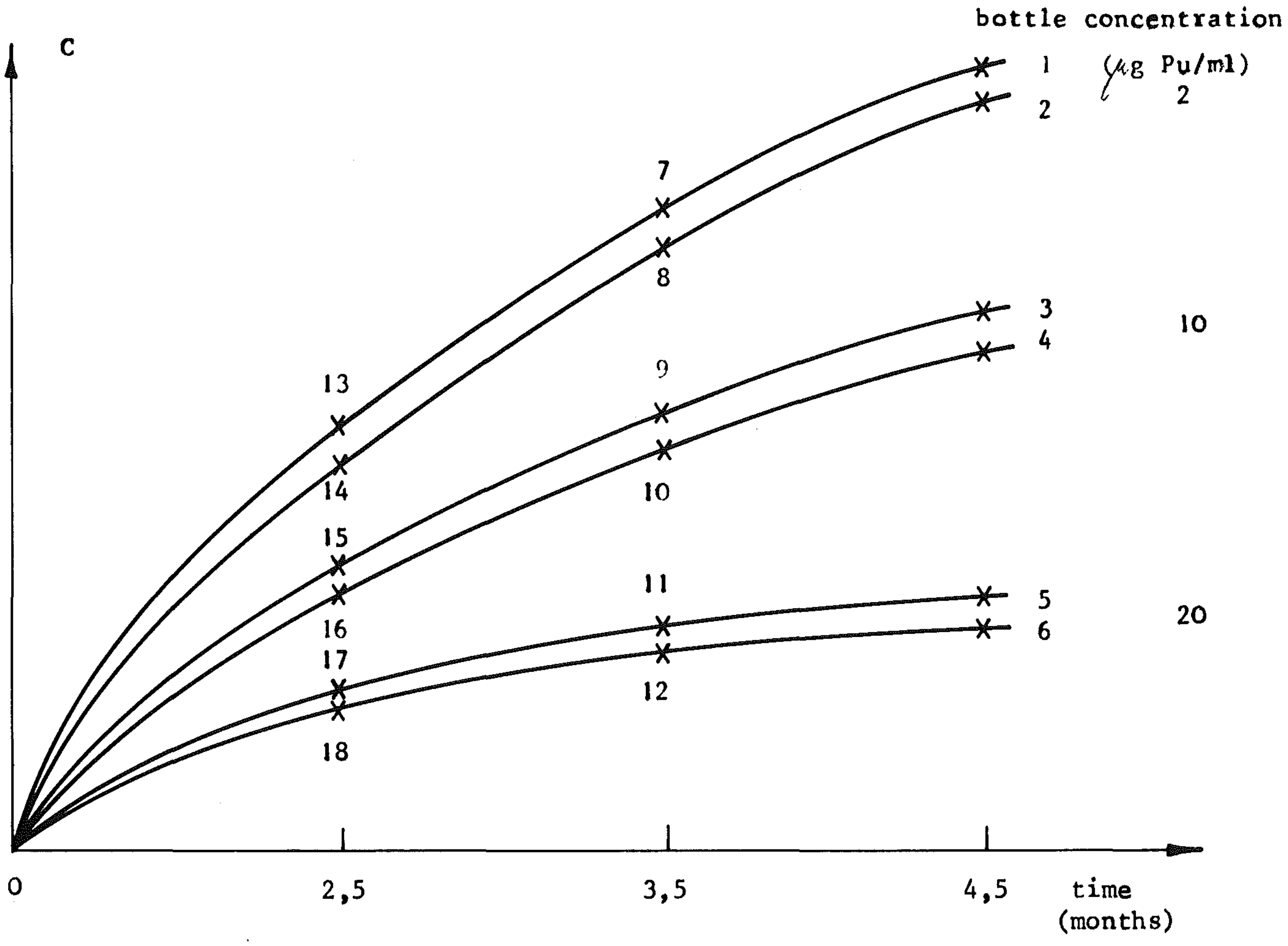
1) Direct mass-spectrometry on unseparated spike, measured Nov. 1973. The corresponding measurements with Pu and U separation (21.11.72) gave:

242/239 47.7 , 67.3 and 51.4 for vials 107, 108 and 109, resp.

240/239 0.426, 0.454 0.423 " " " "

2) Analyzed 15-17.11.1972 and 16-19.1.1973, resp.

3) While the other bottle extracts are eluted from the original sample bottle, this stems from the secondary (2 ml) IFA sample bottle.



x spiking of IFA

Fig. 6-4 IDA-72: Aging Experiment II in a Schematic View
(The given curves are arbitrary assumptions.)

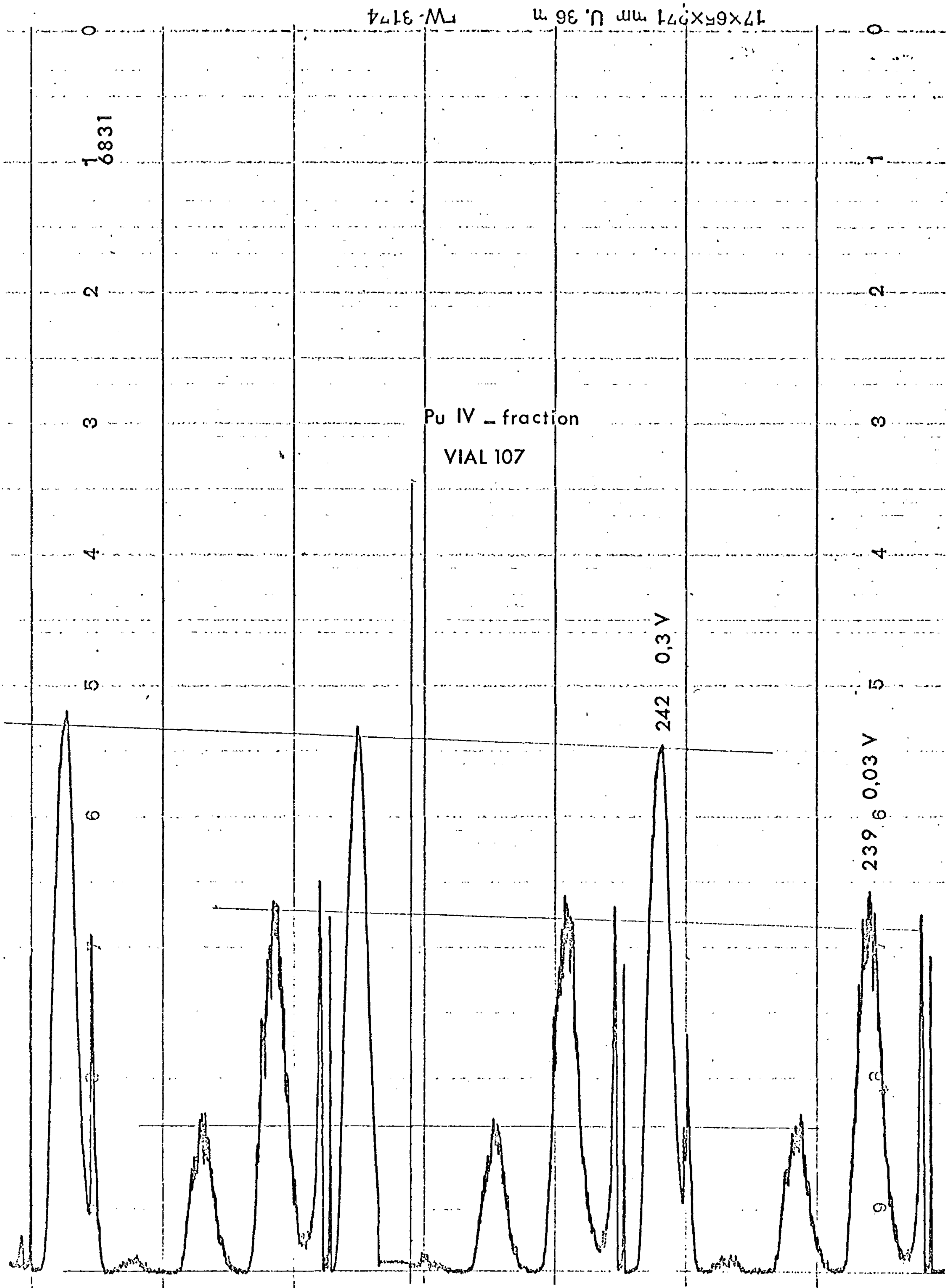


Fig. 6-5 IDA-72: Mass Spectrum of the Pu IV Fraction of the Mixed Spike Solution

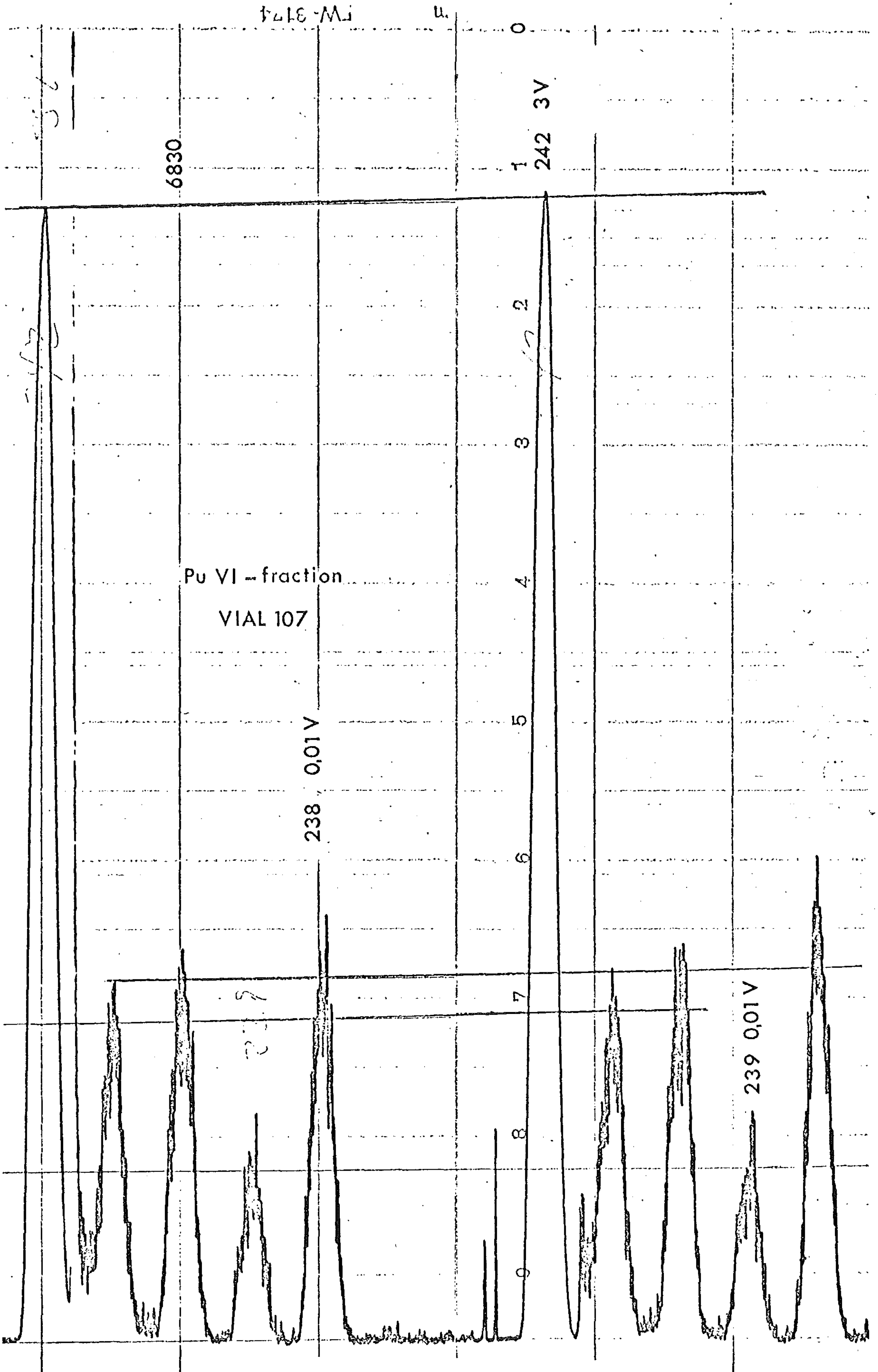


Fig. 6-6 IDA-72: Mass Spectrum of the Pu VI Fraction of the Mixed Spike Solution

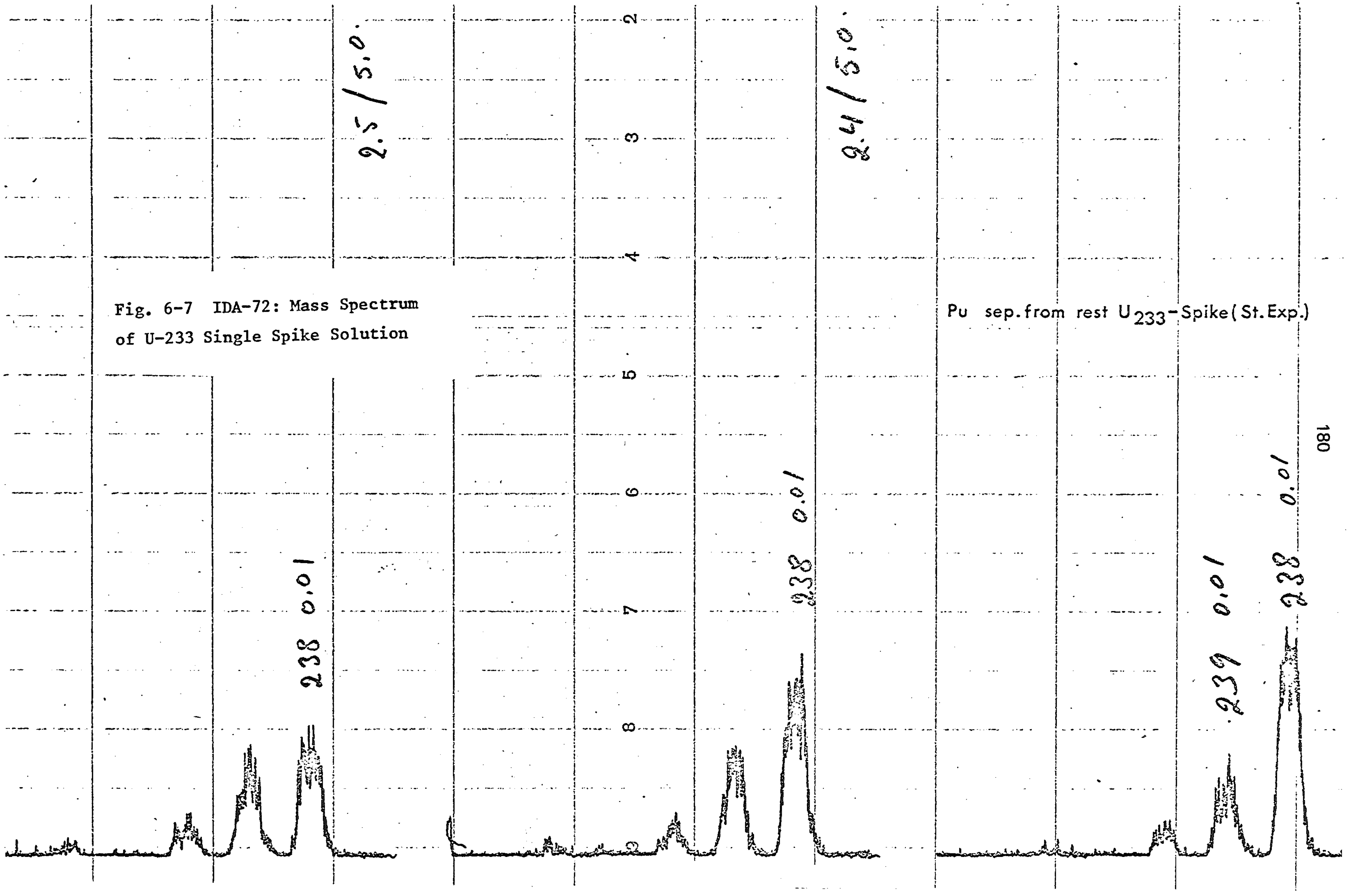


Fig. 6-7 IDA-72: Mass Spectrum of U-233 Single Spike Solution

6.4 Aging Experiment III

6.4.1 Objective

It was the objective of this part of the aging experiment to study the influence of time in the short time range (2-10 days) for active feed solutions, and to test the hypothesis that the aging effects for solutions without fission products, like the R-solution used in the standard experiment, are much smaller or negligible compared to those of active feed solutions like the A-solution of the standard experiment.

6.4.2 Layout and Sample Preparation

For this part of the experiment normal A- and R-solution and normal mixed spike solution as in the standard experiment was used. To cover the time interval of 2-10 days, the spiking of the respective samples was performed at the CBNM/Geel in June 1972 /Vol. II, Par.3/. One additional spiking procedure took place in the Los Alamos Laboratory after 225 days.

6.4.3 Results

The results of this part of the experiment are summarized in Tables 6-5 (uranium results) and 6-6 (plutonium results). In both these tables the results for R-solution (1st block) and A-solution (2nd block) are given. In addition the Figures 6-8 and 6-9 give a graphical presentation of the results. As we could not calculate relative standard deviations for the measuring points, we indicated ± 0.2 % in all cases. The basis for this estimate was the value of 0.17 % calculated as maximum for Pu from the measurements of this laboratory in the standard experiment.

Although this may be too high, especially for uranium, this upper limit was given in order to avoid any overestimation of the concentration differences observed.

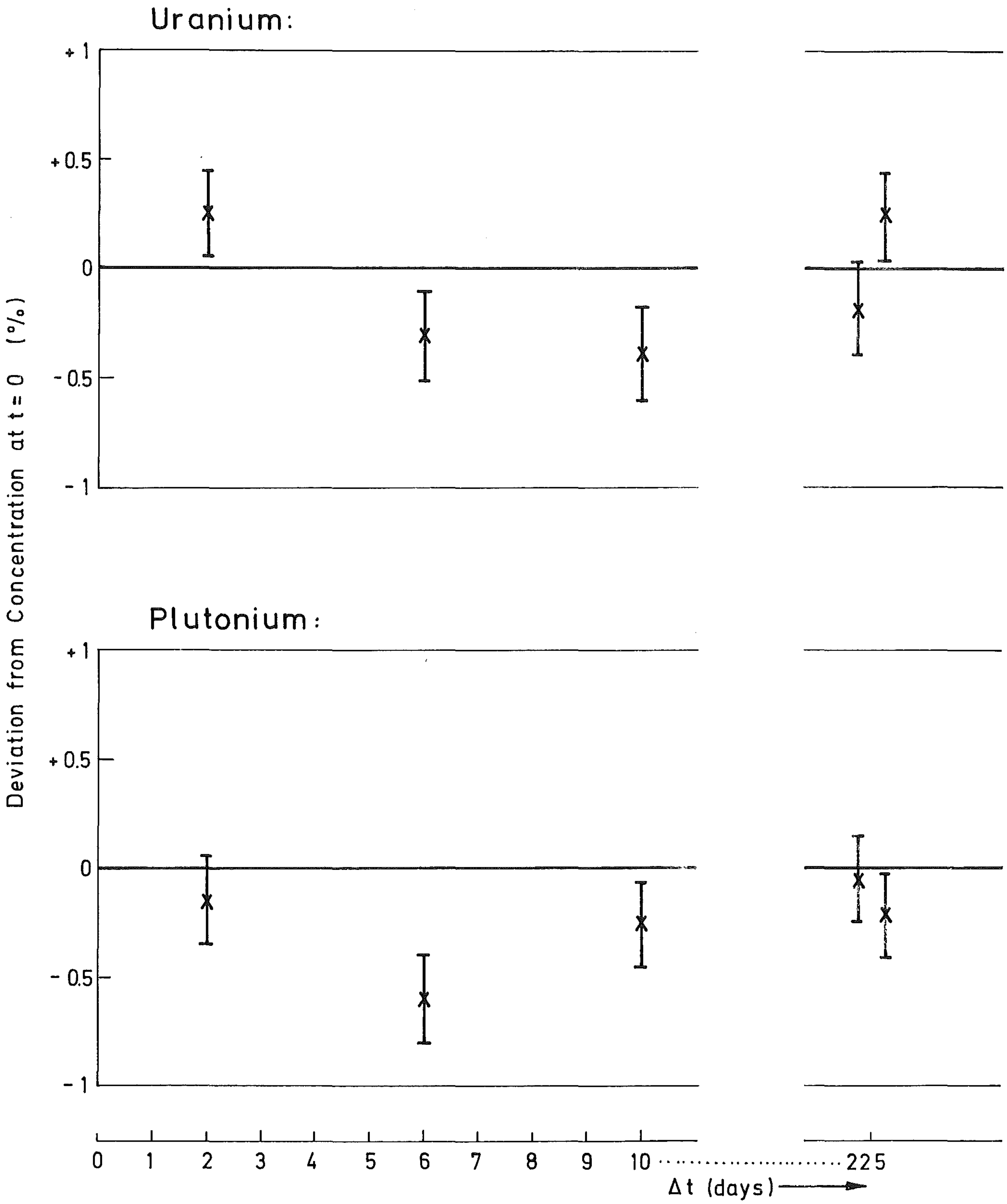


Fig.6-8: IDA-72: Aging Exp. III: Sample "R"

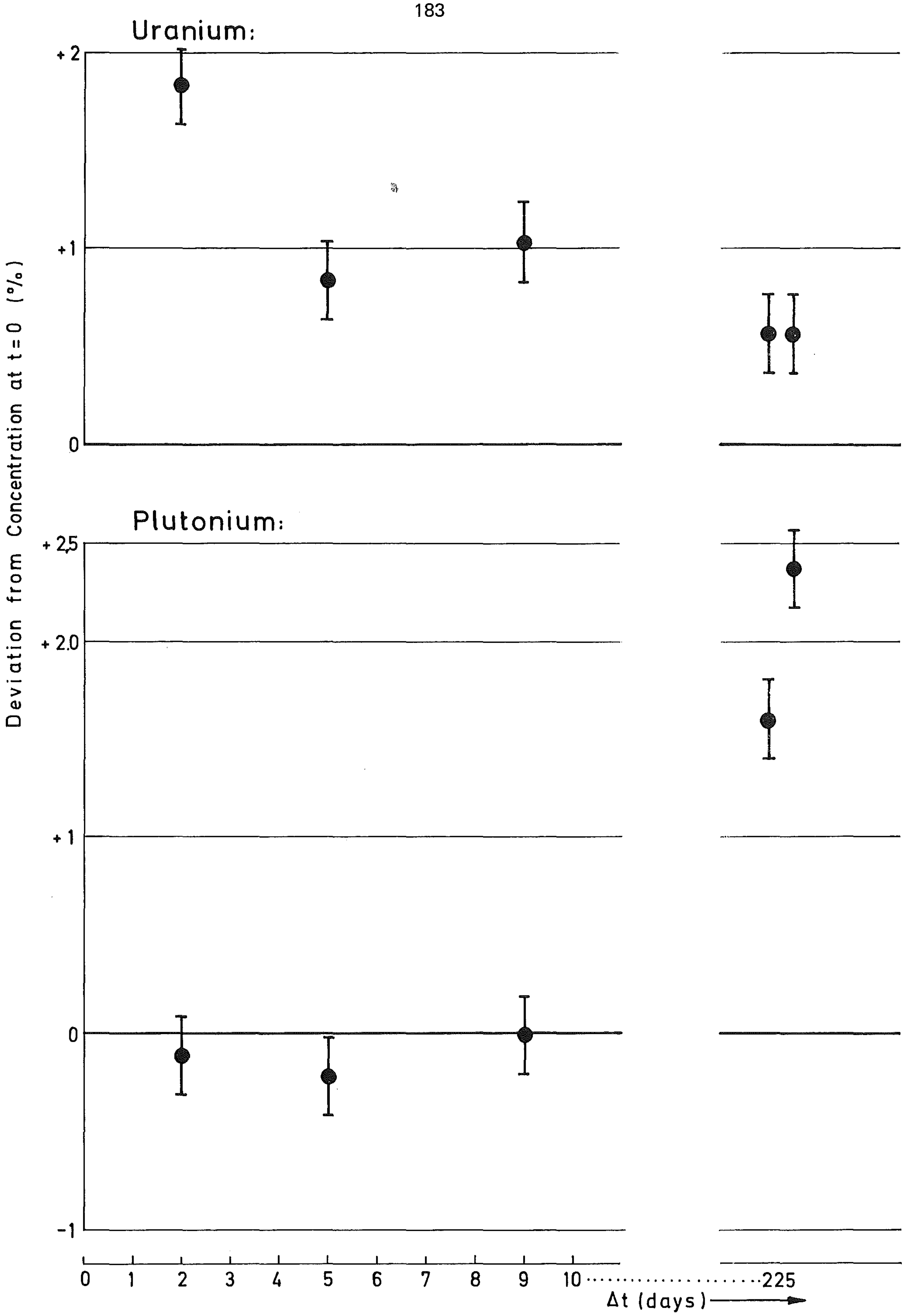


Fig.6-9: IDA 72: Aging Exp. III: Sample "A"

The conclusion can be drawn that the results obtained for the R-sample strongly indicate that this type of sample solutions can be considered as stable in time. This conclusion is rather important, as it would also exclude changes in the concentration of spike solutions by aging - with the exception of evaporation losses in case of unproper storage.

As far as the measurements on the A-sample are concerned, it seems that indeed an instability may be indicated, especially for Pu.

However, as there is also the somewhat high value for the first U-determination, one could hesitate to draw any conclusion on the basis of this limited number of measurements.

Table 6-5 IDA-72

Aging Experiment III/Uranium - Results

Δt [days]	$\frac{U-233}{U-238}$ 1) of spiked samples	$\frac{U-238}{U-233}$ 2) of spike solution	$\frac{U-233}{U-238}$ 2) of unspiked sample	Spike aliquote [g]	Sample aliquote [g]	U-233 concentration of spike sol. $[x10^{18}\frac{atoms}{g\ sol}]$	Calculated U-238 concentration $[x10^{18}\frac{atoms}{g\ sol}]$	Deviation from U-238 concentration at t = 0 3) [%]
R-solution								
2	.7961	.0222	-	1.2124	1.1214	2.093	2.792	+ 0.25
6	.7851	.0222	-	1.2179	1.1490	2.093	2.777	- 0.32
10	.7916	.0222	-	1.2073	1.1302	2.093	2.775	- 0.39
225(R1)	.7468	.0222	-	1.1870	1.1766	2.093	2.781	- 0.18
225(R2)	.7444	.0222	-	1.1869	1.1754	2.093	2.792	+ 0.25
A-solution								
2	.5091	.0222	-	1.2133	1.6660	2.093	2.961	+ 1.86
5	.5220	.0222	-	1.2170	1.6459	2.093	2.931	+ 0.86
9	.5355	.0222	-	1.2005	1.5797	2.093	2.935	+ 1.03
225(A1)	.7148	.0222	-	1.1902	1.1735	2.093	2.922	+ 0.58
225(A2)	.7138	.0222	-	1.1886	1.1734	2.093	2.923	+ 0.62

1) 1 run, mean value of 8 scans

2) Values taken from standard experiment

3) Reference values taken from standard experiment

Table 6-6 IDA-72

Aging Experiment III/Plutonium - Results

Δt [days]	Pu-242/Pu-239 of spiked samples [1]	Pu-239/Pu-242 of spike solution [2]	Pu-242/Pu-239 of unspiked sample [3]	Spike aliquote [g]	Sample aliquote [g]	Pu-242 concentration of spike solution [$\times 10^{16}$ $\frac{\text{atoms}}{\text{g sol}}$]	Calculated Pu-239 concentration [$\times 10^{16}$ $\frac{\text{atoms}}{\text{g sol}}$]	Deviation from Pu-238 concentration at t = 0 [%] [4]
R-solution								
2	1.249	0.0134	-	1.2124	1.1214	2.4594	2.123	-0.14
6	1.230	0.0134	-	1.2179	1.1490	2.4594	2.113	-0.61
10	1.235	0.0134	-	1.2073	1.1302	2.4594	2.121	-0.24
225(R1)	1.164	0.0134	-	1.1870	1.1766	2.4594	2.125	-0.05
225(R2)	1.167	0.0134	-	1.1869	1.1754	2.4594	2.122	-0.19
A-solution								
2	1.061	0.0134	.023	1.2133	1.6660	2.4594	1.701	-0.12
5	1.078	0.0134	.023	1.2170	1.6459	2.4594	1.699	-0.17
9	1.105	0.0134	.023	1.2005	1.5797	2.4594	1.702	±0.0
225(A1)	1.444	0.0134	.023	1.1902	1.1735	2.4594	1.721	+1.63
225(A2)	1.432	0.0134	.023	1.1886	1.1734	2.4594	1.734	+2.38

[1] 1 run, mean value of 8 scans

[2] Value determined by CBNM on mixed spike solution/Tab. 2-1/

[3] Values taken from standard experiment

[4] Reference values taken from standard experiment

7. The Analytical Efforts of the Laboratories Participating in the IDA-72 Experiment

Since the feasibility of a method strongly depends on the efforts which have to be invested when it is applied - and this is specially so for safeguards measures - it was tried to get at least some information on the analytical efforts of the laboratories participating in the IDA-72 experiment.

It is quite clear that it is rather difficult to get realistic and meaningful data in this context because the conditions in the single laboratories vary widely. In the group of participating laboratories there were e.g. research and industrial laboratories, their degree of experience was rather different etc. .

For this reason no request for information on the invested costs was made - but only on the manpower spent for analytical work and data reporting. It should be stressed in this context that the laboratories were asked to work under routine conditions as far as possible. Anyhow, it is not known exactly how far dead times between analyses, instrument maintenance times or times for necessary calibration procedures etc. have been included in the numbers given. This fact should be kept in mind in order to understand the differences in these numbers.

One laboratory gave the important hint that the given times normally don't include the times necessary for the discussion of the experimental outline and the data obtained nor the discussion and the outlining of procedures to be followed for the analytical work.

The following Table 7-1 summarizes the data given by the laboratories.

It was not possible to get complete data from all laboratories, and some peculiarities have been indicated by footnotes.

It is interesting that the given figures for the standard experiment vary between 2.0 and 13.1 man weeks for the analytical work and between 0.2 and 4.5 man weeks for data reporting and that these differing numbers are given by different laboratories. Of course the case of the laboratory with code No. 4 shows that this laboratory has made another subdivision between analysis and data reporting than other laboratories. The laboratory with code No. 21 gave in general larger times than others.

Tab. 7-1: Analytical Efforts

Lab Code	Analytical work load (man weeks)					Data reporting(man weeks)					Overall effort of lab. (man weeks)
	Standard exp.	Self spike exp.	Dry spike exp.	Alu capsule exp.	Total of lab.	Standard exp.	Self spike exp.	Dry spike exp.	Alu capsule exp.	Total of lab.	
2	2.2	1.0	-	-	3.2	1.0	0.2	-	-	1.2	4.4
3	4.8	1.6	1.6	4.2	12.2	2.0	0.9	1.6	3.2	7.7	19.9
4	11.0	1.8	-	-	12.8	0.4	0.2	-	-	0.6	13.4
5	4.0	1.0	-	-	5.0	1.0	0.5	-	-	1.5	6.5
6	9.0	-	1.0	1.0	11.0	3.0	-	1.0	0.5	4.5	15.5
7	Lab. reported: "Samples treated in routine systems and it was not possible to isolate time spent on them"										
8	not reported										
10	5.0	-	-	-	5.0	1.0	-	-	-	1.0	6.0
12	5.0	0.6	-	-	5.6	1.0	0.2	-	-	1.2	6.8
13	5.3	0.8	2.1	2.6	10.8	0.5	0.1	0.2	0.2	1.0	11.8
14	3.0	-	0.7	1.0 1)	4.7	0.5	-	0.1	- 1)	0.6	5.3
15	3.0	0.6	0.8	1.2	5.6	1.0	0.2	0.4	0.6	2.2	7.8
16	2.3	-	-	-	2.3	0.2	-	-	-	-	2.5
17	6.0	0.8	1.5	3.0	11.3	3.0	0.2	0.5	1.0	4.7	16.0
18	2.0 2)	0.4 2)	0.4 2)	1.2 2)	4.0 2)	0.2 2)	0.1 2)	0.1 2)	0.1 2)	0.5 2)	4.5 2)
19	4.0	-	-	-	4.0	0.7	-	-	-	0.7	4.7
20	3.0	-	-	-	3.0	1.0	-	-	-	1.0	4.0
21	13.1	-	3.0	-	16.1	4.5	-	1.0	-	5.5	21.6
23 3)	2.0	-	-	-	2.0	3.0	-	-	-	3.0	5.0
Total	84.7	8.6	11.1	14.2	118.6	24.0	2.6	4.9	5.6	36.9	155.7
mean per lab.	5.0	1.0	1.4	2.0	7.0	1.4	0.3	0.6	0.9	2.3	9.2

1) No results reported on this part of experiment.

2) These figures do not include the actual MS measurements.

3) This laboratory measured U-results only.

Another general comment is that the times necessary for analytical work were on average much greater than those needed for data reporting. Of course the special conditions of this experiment, where the concentration calculations and all error consideration were performed outside the laboratories, has to be taken into the consideration.

On the other hand many laboratories have routine procedures of data processing which could not be used in the IDA 72 experiment so that the influence of this change in the procedure should not be overestimated.

For the additional experiments one can only say that in general the efforts for the evaluation of the aluminium-capsule experiment were about twice as high as those for the dry spike experiment - the reason for this lies in the general outline of these two parts of the experiment. The aluminium-capsule experiment had two parts, one of which was parallel to the dry-spike experiment. In general the efforts for both techniques seem to be equal.

The very high efforts of those three laboratories which have performed the measurements for the aging experiment have not been included in the table in order not to reveal the code numbers. The same is true for the one laboratory in which the U- and Pu-concentrations of the solutions was determined by the X-ray fluorescence method. This latter determination required an effort of 0.2 man weeks for analytical work and 0.2 man weeks for data reporting.

The efforts in context with the aging experiments were given as follows:

		man weeks
Aging exp.	I Ispra	30
" "	II Kjeller	?
" "	III Los Alamos	2.7

The three parts of this experiment are not comparable because of the different number of analyses which had to be performed.

8. Report on the IDA-72 Meeting

8.1 Agenda of the Meeting

Tuesday, February 12th, 1974

Morning session - Chairman : D. Gupta (GfK)

9.15	Welcome address	O. Haxel Scientific Director of the Karlsruhe Research Center
9.30	Interlaboratory tests and safeguards.	D. Gupta (GfK)
9.45	The IDA 72-experiment	E. Drosselmeyer (GfK)
10.25	Sampling at EURICHEMIC, Mol	R. Berg (EUROCHEMIC)
10.50	Sample preparation at CBNM, Geel	Y. Le Duigou (EURATOM-Geel)
11.30	The evaluation of the standard and self spike experiments	W. Beyrich (EURATOM/GfK)

Afternoon session - Chairman : K.L. Huppert (GWK)

14.30	Chemical sample treatment	E. Mainka (GfK)
15.00	α-spectrometry	A. Cricchio (EURATOM-Karlsruhe)
15.45	Aging experiments	E. Drosselmeyer (GfK)
16.30	The evaluation of the dry spike and aluminium capsule experiments	W. Beyrich (EURATOM/GfK)

Wednesday, February 13th, 1974

9.00 Parallel sessions of working groups

A) Chemical sample treatment
Chairman: C.D. Bingham (USAEC)

B) Dry spike and aluminium capsule techniques
Chairman: Y. Le Duigou (EURATOM-Geel)

C) Mass spectrometry-measurements
Chairman: A.J. Fudge (Harwell)

D) Statistical evaluation
Chairman: E. Drosselmeyer (GfK)

Afternoon session - Chairman : S. Facchetti (EURATOM-Ispra)

14.00	Plenum discussion of the results of the working groups A-D	
15.00	Use of solid spike techniques in isotope dilution analysis	P. De Bièvre (EURATOM-Geel)
15.45	SALE PROGRAM: Observation on the determination of U by isotope dilution mass spectrometry	S.S. Yamamura (ANC-Idaho)

Thursday, February 14th, 1974

9.00 Parallel sessions of working groups

E) α-spectrometric determination of Pu-238
Chairman: A. Cricchio (EURATOM-Karlsruhe)

F) Handling of sample material for shipment
Chairman: J. Carter (Oak Ridge National Laboratory)

G) Spiking procedures and standards
Chairman: H. Frittum (IAEA)

H) Aging effects
Chairman: R. Berg (EUROCHEMIC)

Afternoon session - Chairman : A.v. Baeckmann (GfK)

14.00 Plenum discussion of the results of the working groups E-H

15.00 Visits of the Karlsruhe Research Center

a) General sightseeing tour including Department for Waste Management and SNEAK-Reactor

b) Analytical laboratory of the Institute for Radiochemistry

c) Analytical Laboratory of the EURATOM Transuranium Institute

d) Reprocessing plant of the GWK

Friday, February 15th, 1974

Morning session - Chairman:: K.F. Lauer (EURATOM-Geel)

9.30 Final discussion

8.2 List of Participants

A.	v. Baeckmann	GfK Karlsruhe
D.	Bege	KWU Großwelzheim
R.	Berg	EUROCHEMIC Mol
W.	Beyrich	EURATOM/GfK Karlsruhe
P.	De Bièvre	CBNM-EURATOM Geel
C.D.	Bingham	USAEC New Brunswick
G.	Bork	GfK Karlsruhe
J.	Carter	ORNL Oak Ridge
A.	Cricchio	TU-EURATOM Karlsruhe
J.C.	Dalton	BNFL Windscale
P.A.	Deurloo	RCN Petten
E.	Drosselmeyer	GfK Karlsruhe
Y.	Le Duigou	CBNM-EURATOM Geel
U.B.	Eklund	AB Atomeenergi Studsvik
S.	Facchetti	C.C.R.-EURATOM Ispra
D.	Fang	GWK Karlsruhe
N.C.	Fenner	UKAEA-AWRE Aldermaston
H.	Frittum	IAEA Wien
A.J.	Fudge	AERE Harwell
E.	Gantner	GfK Karlsruhe
K.M.	Glover	AERE Harwell
J.	Grison	CEA La Hague
D.	Gupta	GfK Karlsruhe
O.	Haxel	GfK Karlsruhe
K.L.	Huppert	GWK Karlsruhe

K.	Kammerichs	TU-EURATOM Karlsruhe
L.	Koch	TU-EURATOM Karlsruhe
R.	Kraemer	GfK Karlsruhe
K.F.	Lauer	CBNM-EURATOM Geel
M.	Lucas	CEA Saclay
E.	Mainka	GfK Karlsruhe
F.	Mannone	CCR-EURATOM Ispra
J.G.	v. Raaphorst	RCN Petten
P.	De Regge	CEN Mol
F.	Schinzer	NUKEM Hanau
E.	Schultes	GWK Karlsruhe
D.E.	Stijfhoorn	Institut for Atomenergi Kjeller
E.	v.d. Stijl	EURATOM-Luxembourg
R.	Svennen	EUROCHEMIC Mol
K.A.	Swinburn	BNFL Windscale
D.	Thiele	BAM Berlin
F.H.	Tingey	ANC Idaho Falls
C.	Weitkamp	GfK Karlsruhe
S.S.	Yamamura	ANC Idaho Falls

8.3 Working Groups

8.3.1 Conclusions of the Working Group A - Chemical Sample Treatment

Valency adjustment

Valency adjustment by a vigorous chemical treatment is necessary to assure isotopic homogenization between sample and spike, especially for plutonium containing sample solutions. Prior knowledge of the history of sample and spike may not require a vigorous chemical pretreatment; however, it is felt that such a treatment is necessary to assure exchange and to avoid outliers in ratio measurements of spiked samples.

Rather than recommend a particular adjustment method, the group felt that any method must be compatible with the subsequent separation step used in a given laboratory. The general redox methods used by participants, if applied vigorously, should suffice to the needs of homogeneity.

Procedure for U/Pu separation

Individual laboratories have experience with different methods, i.e., solvent extraction or ion exchange. This experience factor was felt to be more desirable than to specify a single method.

Either of the above separation methods, properly used, is adequate to the separation requirements for subsequent mass spectrometric measurements. It was felt more important to cross-check for possible contamination, e.g. 238-U, 241-Am in the case of Pu measurements, by α- or γ-spectrometry.

Procedures for safeguards measurements

The experience factor with a given method in a particular laboratory was felt to override a decision to specify a single method, recognizing the need to assure exchange and to secure a sample of high purity.

Chemical contamination

It was felt that too much concern is given to "organic effects". Variation in filament behaviour due to variations in organic content can be minimized by oxidizing treatments (e.g. fuming in nitric acid) as a routine procedure.Attention to details of mass spectrometer operation should indicate to an operator when deviations from normal response are being experienced.

Sources of all contamination, both chemical and isotopic, must be considered. The attention required is related to sample size loaded onto a filament, to the variation of sample types within a laboratory, to the frequency of running control standards, to the degree that sample-types are, or are not, segregated to specific mass spectrometers, and to the frequency of cleaning the ion-source. It is essential that samples for isotopic analysis exhibit a high degree of chemical purity in order to achieve the optimum in precision and/or accuracy in isotopic measurements.

Critical steps in cross-contamination

Of prime consideration is the cleanest possible chemical operation in any given laboratory. Contamination can occur prior to and/or subsequent to spiking. In either case adverse results will be experienced. Good operational procedures both chemical and mass spectrometric are essential. One-time use of glassware is essential.

Further effort or experimentation necessary

Can the available data be analyzed statistically to show any degree of correlation between a method and the observed results? (To answer this may require more detailed information to be furnished by participating laboratories.)

It was recommended that the existing data be separated to review the "experience factor" involving these kinds of measurements.

Plenum Discussion on the Conclusions of Working Group A

The discussion began with the question whether anything could be said in order to facilitate the decision between the solvent extraction and the ion exchange method. It was stated that the experience a laboratory gets in working with one method is always a strong factor in favour of sticking to this method. The praxis of one laboratory was described saying that the ion exchange method lends itself more to samples being run in parallel whereas the solvent extraction method requires one person on one sample at a time unless the system is automatized.

In the context of contamination problems it was stressed that mass spectrometric measurements require chemically clean samples.

It was asked how far the quality of results is influenced by a cross check of possible contamination by e.g. Am-241 or U-238 and how far not only experience but also the taken effort plays a certain role.

It was concluded that it is just the experience which indicates how much care one has to take using a method and what has to be checked.

The attention was drawn to the importance of a real need for good communication and cooperation between the mass spectrometer man and the chemist.

8.3.2 Conclusions of Working Group B - Dry Spike and Aluminium-Capsule Techniques

- Both methods turned out surprisingly well.

- The procedure for redissolution in the dry spike technique will be revised in respect that the solution will be kept just below boiling.

- The minor difficulties of dissolution of the aluminium-capsules are recognized. There is no objection to local adaptations to overcome such difficulties since normal practice in laboratories are certain to vary somewhat.

- Further work is required on the dry spike technique particularly in regard to the validity of the spike on prolonged storage and in regard to isotopic equilibration of spike and sample. Since in the aluminium-capsule method in situ spiking is unnecessary (i.e. the spike can be added at the time of analysis) any polymerisation during prolonged storage will not disturb isotope mixing. Therefore it is thought that no further work is essential to prove the validity of the aluminium capsule method.

- The dry spike method is in principle acceptable for undiluted samples, but IAEA does not intend to use it for such samples.

- The aluminium-capsule method is suitable for undiluted samples.

- In principle both methods can be used for liquid samples, other than the active feed, involved in safeguards measurements.

- These techniques in simplified form can be used for the Pu to U ratio method of accountancy for input and also for verification by isotope correlation work because weighing is not necessary.

- It is thought that all government authorities would prefer to transport plutonium in solid form rather than in liquid form.

Plenum Discussion on the Conclusions of Working Group B

A comment on the dry spike technique suggested to investigate how long the dried spikes can be stored and whether the isotopic equilibrium which has been shown by the IDA-72 results can be obtained after this time of storage.

In the case of IDA-72 the time interval between spike and sample evaporation was only 24 hours. In practice intervals between some days and several years are to be expected.

Furthermore, it was discussed why the IAEA does not intend to apply the dry spike method for undiluted samples. Some reasons were given: Firstly, there has to be a certain relation between the amount of sample and the amount of spike, this is a question of expenses forU-233 or Pu-242 spikes. Secondly,shipping of undiluted material would mean to ship a lot of radioactivity which would require a shielded cask of high weight and this would increase the shipping cost considerably. Thirdly, the laboratories of the IAEA safeguards network are not prepared to handle material of this activity.

It was pointed out that the procedure of spiking is easier in case of the aluminium capsule technique because the whole capsules are redissolved before analyzing the samples.

8.3.3 Conclusions of Working Group C - Mass Spectrometry Measurements

- All labs represented in group C treated the samples as a routine analysis. Extra work was required to extract the data in the form required by the IDA 72 experiment. Most laboratories used microgram samples and do not think contamination has occured. Labs using nanogram samples also observed no contamination. The Alu-capsule experiment gave only just enough sample material in some cases.

- Filament material contamination is unlikely. Most labs used Re and some pretreated the filament, some do not.
  Reagents are normally checked using a blank run, but contamination is not often found.
  No single cause of outliers is suspected, but the chemical treatment is the most likely cause.
  In the case of Pu measurements poor mixing of the spike is definitely suspect. For safeguards work some standard chemical treatment is recommended.
  The responsibility for mass spectrometry and chemistry should be in the same group.

- No organic contamination was found.

- In general very little increase in accuracy is experienced in going from 10 : 1 to 1 : 1 ratios. Errors increase on going to higher ratios as seen in the graphs of yesterday.

- Machine **bias** is due to:

  a) Ion optics and the position of the sample in the source i.e. loading of the sample and setting of the filament.

  b) Temperature of evaporation. Small samples are normally run at high temperatures. A distillation error can come in by too small samples.

  c) Scanning method. Voltage scanning adds a bias.

  d) Vacuum of the flight path affects the error.

e) Discrimination in an electron multiplier can be up to 2 % but will be a steady value.

These all add up to an instrument bias and as this varies from sample to sample it affects the precision. Not all of the systematic errors and errors associated with these can be eliminated by the use of standards. Various recommendations have come out to reduce these variations and they all amount to a stricter control of analysis conditions.

a) The chemical form of the sample, see mixing above.

b) Control of filament temperature (not just the current).

c) Control of samples size.

All these improve the accuracy, but increase the expense of measurements, too.

- Standards:

  A set of Pu standards, made from mixing pure isotopes, is necessary for Pu measurements. Eventually including 244. Also a Pu 244 spike is desirable.

  In general a standard should have a ratio near to that of the samples to be measured, not 1 : 1 ratio.

  As a matter of convenience and as a political matter Europe should have its own standards. (Action Geel?)

  A standard containing U 233 and 238 would be useful to check the machine bias over a wider range, but this is mainly an academic method. A 233 + 238 spike has not much additional value.

- There is no support for an immediate repeat of the IDA 72 experiment and the value of the SALE and other programs is limited if the results are not to be made fully available. Such interlab comparisons should not be made a basis for qualification as umpires etc. for any safeguards work. The discussion by users has been very useful and should be repeated in say 2 years when it would be useful to consider the form of a new interlab. comparison.

  In 2 or 3 years an experiment similar to IDA 72 would be valuable because in the intermediate time many labs will have obtained spectrometers with better characteristics and will have improved their understanding of instrument bias and sample preparation.

Plenum Discussion on the Conclusions of Working Group C

For the question of the supply of standards different possibilities were discussed, e.g. the exclusive use of NBS produced standards, a cooperative program with the aim to produce a set of standards, rather than many different sets of standards, EURATOM standard material etc.. It was communicated that at a symposium at the NBS it was proposed to supply an international measurement system that would be supported by the contributions of many nations so that all standards would be in context. It was emphasized that the solution of these questions depends strongly on techniques of exchanging samples and having good relations etc..

In addition a principal technical point is involved, namely that to measure the mass discrimination you have to have synthetic standards. It is not possible to judge the value of these because they are unique. So one must at least have a second set made independently in order to be sure to have the right value. And then the question is whether this repetition should be done at NBS and its team laboratories or anywhere else.

It was emphasized that the problem of mass discrimination correction cannot be solved completely by the use of standard materials because of the changes in instrumental conditions from one run to the next.

A hint was given that the Oak Ridge Laboratory has the facilities for seperating isotopes of plutonium on the scale required for checking the possible errors of the machines in the laboratories.

8.3.4 Conclusions of Working Group D - Statistical Evaluation of Data

- **The group began with comparing the methods of statistical evaluation in the SALE and the IDA program. The results were the following:**

  a) In both cases analysis of variances was chosen as the method for the determination of error components.

  2) In both cases scan and run components of the total error were considered as random components, the interlab (or time dependent) error was looked upon as more systematic error (see below, b).

  3) Estimates for error components which came out negative were looked upon as an indication for not significant error contributions.

  4) In both cases the Dixon-criterion is applied for the **elimination** of outliers.

- A list of possible error components in connection with mass spectrometric isotope dilution analysis was put down in order to give **examples** of random and systematic errors and in order to show how very important a detailed discussion with the chemists is for a meaningful planning and evaluation of an experiment:

contribution to error by:	type:
technician	systematic
instrument	"
chemical preparation	random
scan	"
setup (day)	"

- There are totally general models for all forms of mixtures of random and systematic errors. The error analysis of the IDA experiment was a special case. Specially the results on interlaboratory deviations should not be neglected.

- In the final report the RSD components for scan, run and interlaboratory deviation for spiked samples will be given in addition to those for unspiked samples. It shall be undertaken to combine them with the aim to get also the chemical preparation component of the total error which could be specially interesting for chemists. Since in this comparison the difficulties of valency adjustment in the spiked samples are included, one will get an upper limit for this component. Literature on the method will be provided by Dr. Tingey.

- It should be tried to get some more information on possible dilution errors by analysis of a composite set of data on the A, B, C, D, and E samples and comparing the results of the different dilutions to the same nominal values.

- One should check the results on error components by looking at standard deviations instead of relative standard deviations in figures like Fig. 3-28.

  The small absolute values for the concentration on the left side of the figure possibly give a wrong impression on the effects.

- The opinion prevails that the interlaboratory error can be defined either as caused by differences between different laboratories <u>or</u> by differences inside one laboratory caused by persons, instruments, times of the year, systems, calibrations etc.

  For periods longer than about 6 months one has to take into account such a "time component" also inside one laboratory.

  This statement is very important for safeguards and commercial reasons.

Plenum Discussion on the Conclusions of Working Group D

Firstly, it was discussed why the Dixon criterion and not the Chauvenet criterion was used for the selection of outliers. It was pointed out that the Chauvenet criterion has the basis that the measurement values should be normally distributed; the mean value and the variance of this distribution are used for the selection procedure. In case of the Dixon criterion the connection between this assumption of normally distributed values and the selection method is not so stringent.

The reasons for not normal distributions of measurement values were assumed to be varying instrumental conditions as e.g. variation of temperature of the filaments.

The SALE group and the IDA-72 group independently decided to use the Dixon criterion.

It was stated that the decision for the Dixon criterion in this case is not a general one - each evaluation group has first to consider the data material and then to find the appropriate statistical methods.

The next topic of discussion was the question of possible dilution errors. It was stated that the A and B solutions, used in the standard experiment, were produced by quantitative solution, whereas the C and D solutions, used in the aging experiments, were made only semiquantitatively so that no information can be gained from this branch of the experiment. The comparison of concentrations for A, B and E solution - the latter was used undiluted for X-ray spectrometric measurements - have been compiled in Tab. 3-23 together with the results of process analysis at EUROCHEMIC. In addition, the experience of the Mol III-experiment was cited saying that the dilution step was not critical for the method under study.

The next topic of discussion was the question how far it is meaningful to calculate a mean value of the results from different laboratories and how far a statistical interpretation of results can be extended on this basis. It was not tested statistically if all the laboratory mean values belonged to the same population, it was even pointed out that the values coming from one laboratory are not constant in time. This is the main reason for not going more into details by mathematical-statistical methods and for this same reason it seemed not advisable to try to define groups of laboratories which are better or not so good.

8.3.5 Conclusions of Working Group E - α-Spectrometric Pu-238 Determination

The topics discussed by the working group and the conclusions drawn can be summarized as follows:

- The working group recommends that the selectivity of Pu purification in respect to the decontamination from Am 241 must be checked by:

  γ-spectrometry (60 KeV line of Am-241) or by

  repeating the purification or by

  checking the eventual presence of Cm isotopes.

- The uncertainty of Pu isotope half-life values has a small influence on the Pu-238/Pu-239 ratio. Using extreme half-life values (about 1.5% of difference) a deviation of aobut 0.7% has been obtained from the average value for the unspiked sample A. The deviaton is higher in the case of R samples (about 8%) due to the low amount of Pu-238. The bigger incertitude is caused by Pu-238 and Pu-240 values. The group recommends to use the values adopted in the IDA-72 experiment.

- A comparison between alpha and mass-spectrometry results for the Pu-238/Pu-239 ratio has been performed. The working group is of the opinion that in the case of Pu-238 concentrations, as used in IDA-72 experiment, there are no doubts that the α-spectrometric method gives more accurate values for the Pu-238/Pu-239 ratio. In the case of higher Pu-238 concentrations the two methods must be correlated experimentally.

- Small problems are caused by overlapping of tails when electrodeposited sources are used. Unfortunately only three labs used this method for the experiment. The 8 other labs have used a source prepared by direct evaporation which gives more intensive tail effects. The working group is of the opinion that thin α-sources giving a resolution lower than 25 KeV should be used in order to avoid the tail problem.

- The working group thinks that the results of the IDA-72 experiment may be influenced by the individual method of data handling. For safeguards purposes an additional experiment is proposed just to check the different methods of peak-surface calculations. Typical poor resolution spectra of different isotopic ratios should be distributed to participating laboratories and the results should be compared with those obtained on infinitely thin sources of the same isotopic ratios.

Plenum Discussion on the Conclusions of Working Group E

The discussion began with the question of the best known value for the half life time of Pu-238. The value 87.7 years has been used which is about the average of the values which can be found in literature. It was pointed out that the deviations of these values are important compared to those of the half life times of other Pu-isotopes. For Pu-239 e.g. a deviation of 0.7 % is found between the different values published in literature.

It was communicated that there is a group of laboratories in the United States which has a continuing program for remeasuring the half life times of purified isotopes. Dr. R.K. Zeigler of Los Alamos was mentioned as one of the authors of a note published recently by this group. Reference was also made to the KFK report Nr. 1852 where the results of european reevaluations are collected (page 40) together with a list of references.

It was also mentioned that in the Los Alamos program a peculiar difficulty showed up in determining the Pu-241 half life by direct decay measurements: Depending upon the isotopic enrichment of the samples there are two half life values coming out and there is not yet an explanation known for that phenomenon. The difference is of the order of nearly 1 %.

It was reported on measurements of the Pu-239 half life by calorimetry which show a tendency to give a value which is somewhat lower than the value of $\sim$24000 years currently accepted.

8.3.6 Conclusions of Working Group F - Handling of Sampling Material for Shipment

Several laboratories found that some attack of the top of transportation bottles had occured. Over short distances this appeared to be satisfactory. For longer distances improvements are necessary. The comments of two laboratories are included to illustrate some of the difficulties encountered.

Lab A

"The method of sealing the samples in their containers should be improved in a future experiment or when samples are sent to laboratories for checking. Several of the capsules showed signs that the solution had leaked out and the R unspiked bottle for the standard experiment was completely empty. The outer containment was satisfactory and no external activity was observed, but the capsules containing the solutions had failed to seal in several cases".

Lab B

"In unpacking sample A (unspiked) of the standard experiment it was notized that the sealed plastic bag appeared wet on the inside and that 2 drops of a yellowish liquid were visible. The tube appeared to be intact, the cap tight, and the sealing tape neither wet nor discolored.

The threaded part of the tube containing sample A (spiked) was broken while attempting to unscrew the cap. Neither sample loss nor contamination occurred as a result".

Quantity of material: The advantages of only transporting small quantities on grounds of cost and safety are obvious. However, individual laboratories have different requirements of amounts used. All future shipments and containers should conform to IAEA regulations. Some countries have also individual additional regulations for the transport of radioactive materials.
Standardized containers acceptable to all countries should be developed and also the administration requirements, as far as possible, be standardized.
The transportation of small quantities should not be subjected to the same requirements of administrative clearance as large quantities.

The results of the self spike experiment indicate that the transportation of non-active solutions can be carried out without any serious losses.

Plenum Discussion on the Conclusions of Working Group F

It was added to the report of the working group that in the whole experiment only one sample vial arrived empty and in no case was reported that a vial was broken.

Upon request the IAEA reported on the experience that the problem of transportation can be quite difficult due to the fact that the IAEA has some regulations which are not always conform with the national regulations of the states. These differences occur mainly with respect to sample containers, i.e. the outside containers in which the tiny glass or plastic vials for the samples are sitting. It is being tried to standardize these containers.

It was asked whether or not the use of dry spike techniques could make the efforts for transports easier or even obsolete. A preference for dried samples was clearly expressed. It was accentuated that the situation could be different for solutions not coming from the input tanks of reprocessing plants, as e.g. products in form of plutonium nitrate solution and uranyl nitrate solution which have to be shipped in liquid form. However, an EURATOM laboratory stated to have successfully worked on the basis of dry samples for all types of material.

8.3.7 Conclusions of Working Group G - Spiking Procedures and Standards

- Outliers are due to a number of unknown variables which require additional investigation of the individual laboratory efforts.

- a) All of the methods are theoretically valid. The practical applicability has to be considered on a case by case basis - relating to plant convenience, cost, safety, transportability, etc. Bringing the spike to the plant permits the assay result to be "frozen" at the time and place of sampling.

  b) Use of reference solution for spikes historically has been the most straight forward in the laboratory. Non-solution methods are evolutions in time and practice.

  c) Solutions are more difficult to manipulate - requiring more frequent calibration, and suffer from packaging and transportation difficulties. Solution spikes are generally used at the analyzing laboratory to which the samples are shipped.

  d) Non-liquid spikes require more additional steps at the plant than liquid spikes. The preparation of the "solid spike" however requires fewer steps than the "dry-spike" or "aluminium-capsule" method.

  e) The average cost of all methods is comparable - being mostly labor.

  f) If conditions are properly chosen no significant difference should appear in the results. This conclusion is based on obervations (excluding outliers) of IDA-72 and the solid spike method.

  g) Regarding safeguards, the comments in an apply. In addition, it may be noted that the use of non-liquid spikes imposes more on the plant than the liquid spike method. Non-liquid spike operations in a plant make the safeguards inspection more dependent on plant personnel and equipment.

- Distribution of Standardized Spike Solutions

  World-wide availability of an agreed-upon reference is a desirable position. The use of such a reference material should be at the option of laboratory unless legislated by some authority.

Plenum Discussion on the Conclusions of Working Group G

The only topic of discussion was the question how far undiluted samples can be maintained. Additional dilution steps are somewhat adverse to some procedures as they are now used in the plants, on the other hand the aluminium capsule technique has not been performed with undiluted samples in this experiment.

8.3.8 Conclusions of Working Group H - Aging

- Only input solutions were discussed
- Both U and Pu is included in the discussion, but as expected Pu dominated the discussions
- Trivial phenomena as evaporation and isotopic decay did not enter the discussion
- Level to be detected (refer to IDA-72) >> 0.5 %
- Time interval to be studied should in eventual new **experiments be extended;** may be to several years. The analytical effort should then be increased to a higher number of analyses equidistant in time, with parallel standardisation measurements
- Short time effects were discussed, but one concluded that it would be extremely difficult to study the phenomena experimentally (0.5 - 10h after sampling)
- A defined aging phenomen is plating-out on vial surfaces (recoil?; ion exchange?) and on **tank-pipeline** surfaces
- The chemists in the working group feel that polymer Pu formation is unlikely in acid solutions above 1 M (IDA 72 used 2.5, 5 and 8 M) even when steam jet transfers are used to the input tank.
- Organic compounds (traces?) will always be found in the acid used for **dissolution of the fuels.**

  Degradation and therefore behaviour relative to U and Pu may change with time and give "aging" effects.
- Conventional MS with separation compared with MS done without separation could be a possible approach to gain more information about aging.
- If aging experiments are undertaken in the future, the specific activity of two solutions should vary widely (diluted, undiluted).
- The working group is reluctant to draw any conclusions on the Aging experimentI A trend is recognized. However, **the group believes** that only one acidity (2.5 M- close to reprocessing conditions) would be sufficient in an eventual new experiment.

- The working group is also reluctant to draw any conclusions on aging experiment II.

- The working group is also reluctant to conclude on aging experiment III.

- For all aging experiments the group feels that the number of data is insufficient.

- Further experiments on aging have to be carefully planned with the aim to eliminate all suspected error sources.

  Such experiments, if performed for safeguards and/or accounting purposes will have to be tailormade to the sample type (diluted, undiluted, taken to dryness).

- The working group feels that solidified samples (aluminium-capsule technique, solid spike technique) are far less subject to aging phenomena than liquid samples.

Plenum Discussion on the Conclusions of Working Group H

The discussion began with the comment that significant aging effects can be found in solutions with high plutonium concentration as e.g. the end product of a reprocessing plant. The studies of aging in the framework of IDA-72 had been limited to solutions related to the experiment as a whole in order to have a narrower subject.

There exist aging phenomena besides the trivial effects of evaporation and isotopic decay. Some experience exists on plating-out on vial surfaces (recoil, ion exchange) and on tank-pipeline surfaces.

It was asked which real effects are likely to be the causes for nontrivial aging effects. It could only be said that there is no definite evidence for such causes, the effects are that there are polymeric species which cause difficulties in chemistry. Specially traces of organic compounds will always be found in the acid used for dissolution of the fuels. Degradation and therefore behavior relative to U and Pu may change with time and lead to aging effects. It is felt that polymer Pu formation is unlikely in acid solutions above 1 $\underline{M}$. In this context also the question of higher concentrated or undiluted impure solutions was discussed.

It was stated that according to IDA-72 results effects < 0.5 % cannot be detected.

Again the question came up whether it is worthwhile to study aging effects in liquid solutions knowing about the possibilities of dry spike techniques.

It was stated that from a purely scientific point of view aging studies on different types of samples would be interesting. But it would mean a tremendous analytical effort to obtain meaningful data. So it was proposed to begin with defining a sample system for safeguards purposes or for umpire control samples first and then decide upon an eventual new aging experiment. The time interval should be extended compared to IDA-72;maybe to several years. Also short time effects (0.5 - 10 h after sampling) would be interesting, but it seems to be extremely difficult to study them experimentally. It was also proposed to compare conventional mass spectrometry measurements with separation with measurements done without prior separation in order to get more information.

8.4 An Accurate Procedure to Safeguard the Fissile Material Content of Input and Output Solutions of Reprocessing Plants

(by P. de Bièvre and J. van Audenhove)

Safeguarding reprocessing plants requires physical sample taking and accurate determination of fissile material contained therein, in order to support effectively any administrative inspection and to back up efficiently the safeguards authorities.

Possible procedures for such sample takings and determinations involve

1. transfer of (hot) samples (out of the hot cells) to (hot cell) facilities for analysis or
2. quantitative decontamination of samples (no U or Pu loss allowed) or
3. analysis within shielded cells (hot samples).

These operations are performed at considerable cost and problems with regard to keeping the identity of the sample with respect to its U and Pu isotopic composition as well as to its U and Pu element concentrations. Moreover most analyses are performed at a certain distance in time (no immediate analysis) and location (safeguards measurement laboratory), hence yield analysis values applicable - as all analysis values - to time and place of the analysis and not necessarily to time and place of sample taking. The latter requirement is however basic to any safeguards inspection system.

In the framework of the measuring support to the Safeguards authorities of the European Economic Community (Contrôle de Sécurité, Luxembourg) we are giving since 1966, we have established at the CBNM a procedure to circumvene the disadvantages quoted, guaranteeing at the same time to these Safeguard Authorities, values for fissile material content which are essentially free from most error possibilities arising during the time between sample taking and analysis.

The procedure runs as follows:

1. The Safeguard Authorities communicate to CBNM very rough estimates of U and/or Pu isotopic and chemical concentrations of the dissolved fuel they want to sample for a check analysis.

2. CBNM prepares and delivers to the Safeguards inspector appropriate solid spikes (U metal or U/Pu alloy) suited to the particular problem concerned, and which can be handled easily, safely and quantitatively. These spikes are accurately defined with respect to U and Pu content and isotopic composition by

   a) their quantitative preparation (levitation alloying)
   b) isotope dilution assay against primary standards
   c) mass spectrometric isotopic analysis.

3. A spike is added to a weighed sample of the solution to be investigated in the (hot cell of the) reprocessing plant and dissolved.

4. After homogeneization of the solution a fraction of it is decontaminated from fission products and transferrred out of the hot cell (no quantitative operation required).

5. The inspector sends the spiked sample containing only mg amounts of U and µg amounts of Pu to CBNM (samples are radiation-free since free from fission products).

6. The procedure is performed in duplicate i.e. two different solid spikes (different weights) and two different samples are used. A separate non-spiked sample is taken for U and Pu isotopic analysis.

After mass spectrometric measurements, coinciding results of the duplicate spiking combined with previous spike definition allow CBNM to certify accurately to the Safeguards Authorities the fissile material concentration (U and/or Pu) at the time and place of sample taking.

Examples:

	Content mg U/g	Content mg Pu/g	Isotopic Composition	Weight %
1st example:				
1st spiking	186.5	1.238	U-234	0.0149
			U-235	1.8702
			U-236	0.2269
2nd spiking	187.2	1.252	U-238	97.8880
Certified	186.9	1.245	Pu-238	0.426
			Pu-239	75.761
			Pu-240	15.130
			Pu-241	7.606
			Pu-242	1.077
2nd example:				
1st spiking	166.8	0.6281	U-234	0.0041
			U-235	0.2530
			U-236	0.0689
2nd spiking	166.2	0.6221	U-238	99.6740
Certified	166.5	0.6251	Pu-238	0.167
			Pu-239	69.324
			Pu-240	24.198
			Pu-241	4.857
			Pu-242	1.454

Characteristics of the procedure:

1. results are certified for time and place of sample taking and not time and place of analysis
2. small amounts of sample & spike results in easy handling
3. hence no material cost
4. and insignificant transportation cost

5. and insignificant radiation risk during transport
6. flexibility: fits the particular fissile material concerned
7. reliable: see figures: up to now not one major error occured (has been operational in reprocessing plants since beginning of 1972 after extensive laboratory-testing)
8. tamperproof: coinciding results of duplicate isotope dilution provide unequivocal conclusion.

8.5 Summary of the Final Plenum Discussion

The chairman of the session presented an extensive survey on the main results of the evaluation and the comments given in the working group sessions of the days before.

The most important statements and recommendations mentioned and proposed as subjects for the following final plenum discussion can be summarized as follows:

Mass Spectrometry:

- on an interlab basis, measurements can be done with a precision of 0.7 to 1 % at this time

- if these values are not reached, unsatisfactory instrumental operation is considered as the most probable reason.

- improvement of error limits can be expected during the next years due to the installation of more modern instruments in the laboratories.

Chemical Sample Preparation:

- The numerous outlier values observed are most likely caused by cross contamination in any of the analytical steps and by unsuitably chosen valency adjustment and separation procedures.

- redox and purification procedures should be used which are sufficiently strong to assure quantitative performance even if samples of unusual composition have to be analysed

- sample preparing chemistry and mass spectrometry should favourably be done under the same responsability.

New Techniques of Sample Conditioning:

- The non-liquid spiking techniques (dry spike and aluminium-capsule method, use of metal alloy spikes) should be used wherever possible because of their advantages concerning sample representativeness and stability as well as for facilitating transportation.

Transportation:

- For questions of standardizing the container types, authorisation and administration in different countries the existing experiences of e.g. Amersham, the CEA etc. and IDA should be considered, although the conditions of the IDA-experiment were somewhat particular.

Aging Effects:

- As the use of liquid sample material cannot be avoided completely, aging effects remain of importance at least for "chemically difficult" solutions. However, it is proposed to study them on an academical rather than on a technological basis.

Evaluation of Data:

- Is it meaningful to try to obtain more detailed information from the data by more detailed evaluation even if this necessitates revealing of codes at least partly?

Future Work:

- As it seems that all participants find the work which was done in IDA-72 useful and efficient, there is the question whether or not this type of method evaluation should be continued in the future, in which fields, and by which organizing structure.

- In this context, the suggestion of an ad-hoc group for the evaluation of α-spectra should be discussed.

In the following plenum discussion, no additional comments were made concerning the topics mass spectrometry, chemical sample preparation and aging effects.

In connection with the application of the new techniques of sample conditioning in practice, the necessity to limit in-plant operation steps to a minimum was underlined. A clarification was given that the problems of sample instability can also be avoided by the use of dried samples, not only by spiking with metal alloys.

The suggestion was made that those laboratories in which these new techniques were developed should prepare more detailed descriptions on the recommended procedures as at least in a few cases difficulties were observed.

Several remarks were made in regard to the question of further evaluation of data necessitating at least partly a revealing of codes. Although the freedom of discussion on the working level was advocated and appreciated, breaking of codes was not recommended as the guaranteeed anonymity was considered as fundamental for the success of the experiment.

The rather extensive discussion on future work was strongly influenced by the favourable valuation which was given in general by the audience to the performance of the IDA-experiment and the information obtained. It was stated that not only the aim of determining the "state of the art" concerning isotope dilution analysis could be reached but that the individual laboratories could recognize the weak points of their own procedures and can now try to improve them. It was appreciated to have a forum for discussions at the working level specially for taking the aspects that concern people who have to operate safeguards and translate them into realism. A new meeting after two or three years was proposed to pool again the common knowledge gained. This suggestion was mainly supported by the mass spectrometrists.

Concerning further experimental collaboration, two types of problems were identified:

Firstly, problems of limited scope for which specific groups of interest exist and which can be solved with relatively small effort in the immediate future. The suggested ad-hoc-group for α-spectra evaluation is an example for this. The existing evaluation group of IDA-72 will give the necessary organizational structure for such activities.

Secondly, somewhat more advanced into the future, further experiments for methods evaluation, either in isotope dilution analysis again or on other fields like e.g. burnup determinations or minor isotope techniques, if there exists sufficient interest. Also for these aspects it was proposed to rely on the existing evaluation group at the present. On long terms, however, a broader basis was considered necessary for these activities. In this context it was strongly emphasized that the way and the level the IDA-experiment was executed as a method evaluation program should be maintained and that the fruitful collaboration on the laboratory working level should not be killed neither by administrative bureaucracy nor by any conjunction with laboratory quality programs.

A considerable part of the discussion pertained to standards and reference materials. Although no final conclusions could be reached, some princple problems and opinions stated are compiled in the following:

Types of Standards needed:

Whereas the situation on uranium standards was considered as satisfactory, additional demands exist in the plutonium field and maybe for fission products. However, no exact specifications could be given at the meeting directly.

It was pointed to the inquiries made on the actual needs by the USAEC and Harwell. Within the EEC, these questions shall now be handled by the Bureau of Reference Materials at Brussels.

Quality:

In respect to the other error sources involved in the analyses, the quality of the existing NBS standards was considered as satisfactory for safeguards purposes. There was some indication that research laboratories might be interested in standards of higher accuracy.

Availability:

The difficulties in getting standard materials within reasonable periods of time or in obtaining isotopes as e.g. Pu-244 were criticized.

In this context as well as from the strictly technical point of rechecking the question was raised whether or not standard materials should be developed and made available also by European organizations in spite of the considerable efforts such activities would necessitate.

9. Summary on the Results and Experiences of the Experiment IDA-72

9.1 Errors Involved in Mass Spectrometric Isotope Dilution Analysis

9.1.1 Errors up to 50% and more were observed in about 20% of the concentration determinations of plutonium, difficult to detect as such by the laboratories themselves.
Cross contaminations with plutonium of other isotopic composition and not sufficiently rigorous procedures for valency adjustment of the plutonium in spike and sample solution are obviously the reasons.

In the determination of uranium concentrations due to the more favorable conditions with this respect, such "outlier" values were not observed. /Par. 3.5.2, 3.5.3 and Vol. II, Chapter 6/.

9.1.2 Concerning the isotopic ratio determinations by mass spectrometry, 4% of the laboratory means obtained from uranium measurements and twice as much in the case of plutonium were outliers, again in general difficult to detect as such by the laboratories themselves. As far as chemically uniform solutions are concerned, cross contaminations are probably the reason in most cases /Par. 3.2.1 and 3.2.2/.

9.1.3 After rejection of the outlier values mentioned above, estimates for the relative standard deviations of three error components in the isotopic ratio determinations were calculated (scan, run and interlaboratory deviation) /Par. 2.5/.
In a first approximation, the relative standard deviations of these three error components are of the same order of magnitude and no significant difference was observed for uranium and plutonium.

For isotopic ratios above 1 % the relative standard deviations are in general below 1 % and increase to the order of 10 % for isotopic ratios of about 0,01 %.

The most important mass spectrometric error contribution to concentration determinations is the interlaboratory deviation of the ratio measurement for spike isotope/reference isotope of the spiked sample solution. This ratio is in general about 1. A relative standard deviation for the interlaboratory deviation of 0.8% for uranium and of 0.5% for plutonium were found /Fig. 3-28 and 3-29/.

9.1.4 For the Pu-238 determination α-spectrometry was preferred by the majority of the laboratories. For isotopic concentrations of about 1.5%, values around 1% were calculated for the relative standard deviations of precision and interlaboratory deviation. They increase with decreasing Pu-238 content of the sample. Specificly at low Pu-238 levels a considerable number of outliers was observed, caused mainly by cross contamination or insufficient separation of Am-241 /Par. 3.3.2 and Vol. II, Chapter 8/.

9.1.5 Calculating the relative isotopic composition as obtained by the individual laboratories for the three solutions under investigation, unsatisfactory results were obtained for 7% of the uranium and 24% of the plutonium data. This is explained by the fact that knowledge of all isotopic ratios is necessary for these calculations, and therefore, considerable errors are brought about if one of the single isotopic ratio determinations is an outlier or has not been measured at all /Par. 3.4/.

9.1.6 After rejection of all outlier values, the relative standard deviations of the error components indicating precision and interlaboratory deviation for concentration determinations, performed under different experimental conditions, could be estimated. 0.7 to 0.8% were obtained for the interlaboratory deviation in the case of uranium as well as of plutonium if the spiking procedure is included. The values for the precision are in general somewhat lower, specificly if synthetic sample material without fission products is analysed /Tab. 4-8/.

9.1.7 For the total error of an element concentration determination in a diluted active feed solution obtained from double analysis in one laboratory (including the spiking procedure) estimates of 0.9 and 1.0% were calculated for uranium and plutonium, respectively. These figures are reduced by about 0.15% if the concentrations are stated for the main isotope only so that error contributions by the isotopic composition determination are avoided /Par. 4.4/.

9.1.8 Separate quantitative estimation of the errors involved in the spiking procedure is complicated by the fact that they are partly compensated by the spike solution calibration if this is made by the same laboratory which performed the analysis as it is usually the case in practice.

The results of this experiment indicate no significant contribution of the spiking procedure to the total error of the concentration determination in the case of uranium. For plutonium, the contribution to the total error of a double analysis performed by one laboratory was estimated to be 0.2% /Par. 4.4/.

9.1.9 The best mean values of all concentration determinations performed in this experiment for a synthetic reference solution (calculated after rejection of outliers) deviate from the theoretical values by nearly - 0.5% for uranium and - 0.2% for plutonium.

Besides the uncertainty of the mean value of the analytically determined concentration values, errors in the spike solution concentration, the aliquotation procedure and the uncertainty of the theoretical concentration (< 0.1%) contribute to these differences /Par. 3.5.2 and 3.5.2/.

9.1.10 There is no indication that Pu/U concentration ratios can be determined more accurately than the concentrations of the individual elements /Par. 3.5.5, 4.2, 5.1.2, 5.2.2 and 5.3.2/.

9.2 Capability of New Techniques for Sample Conditioning

The results in testing the new developed non-liquid techniques for sample conditioning (dry spike technique /Vol. II, Chapt. 4/ and aluminium-capsule technique /Vol. II, Chapt. 5/) were very favourable: Neiter any significant systematic error was observed due to the application of these techniques nor any significant increase in the spread of the laboratory means (i.e. mainly the interlaboratory deviation) even in spite of the fact that the number of analytical steps contributing to the total error in this case was higher /Par. 5.4/.

9.3 Stability of Liquid Samples

Because of the limited number of available data the results of the experiments on aging are very restricted. The clearest result was obtained on a reference solution free from fission products. No change in the sample composition is indicated after a period of more than 7 months - this is of some importance with respect to the storage of spike solutions /Par. 6.3/.

9.4 General Experiences

9.4.1 Transportation of liquid sample material is rather troublesome from the technical point of view and expensive. Furthermore, considerable delays are caused by the administrative requirements, varying from country to country /Par. 2.3/.

9.4.2 Data transmission without mistakes in figures and without misunderstandings in definitions is a serious problem /Par. 2.5/.

10. Conclusions and Recommendations

10.1 Analytical Aspects

10.1.1 Cross contamination is a basic problem and requires maximum attention. Throwaway parts have to be used wherever possible. In order to increase the probability that cross contamination is detected by the laboratory itself, samples should be subdivided immediately after their arival at the laboratory at least into two parts which are passed through the individual analytical steps as independently as possible. Limits for the acceptable deviations can be estimated from the results of this experiment.

10.1.2 Concerning sample preparation for plutonium concentration determinations, extreme care has to be taken that redox and purification procedures are used which are sufficiently strong to assure quantitative performance even if samples of extraordinary composition have to be analysed. Again, limits for the acceptable deviation of repetition analyses can be estimated from the results of this experiment. Errors caused by unsatisfactory valency adjustment can be distinguished from cross contamination by comparing the relative standard deviation of the ratio spike isotope/main isotope with those of other isotopic ratios, presuming that a nearly monoisotopic spike material was used.

10.1.3 Attention should be payed to the fact, that the determination of isotopic compositions - e.g. for calculating element concentrations of uranium or plutonium - necessitates the correct measurement of all isotopic ratios contributing significantly. Therefore, possibilities for satisfactory determination of Pu-238 and quantitative separation of Am-241 are absolutely necessary.

10.1.4 Presuming no outlier conditions exist due to one of the reasons mentioned above, the limits of error are essentially determined by the mass spectrometric measurements. Careful corrections of mass discrimination are necessary, specificly if only isotopic ratios or compositions have to be determined, or in the case of concentration determinations, if the spike solution used was not calibrated by the analysing laboratory. Still demands exist for isotopic standards suitable for these calibrations, mainly as far as plutonium is concerned. However, a considerable part of the mass spectrometric error is caused by the change of operating conditions from run to run, uncorrectable by calibration. Therefore, instrumental stability has to be controlled carefully. It is recommended to use the mean values obtained in this experiment for the scan and run component as reference.

10.2 Safeguards Aspects

10.2.1 For analytical results determined by one laboratory only, the possibility of extreme errors caused by cross contamination can never be excluded.

10.2.2 If specificly the plutonium concentration determinations by any laboratory are suspect, the application of sufficiently effective valency adjustment procedures has to be checked.

10.2.3 If no outlier conditions exist, the relative standard deviation of a concentration value determined by double analysis within one laboratory is about 1.0% (1σ) for uranium as well as for plutonium. This means that with the present state of the art differences of 2% in the concentration values determined by two laboratories on the same sample can easily be obtained.

10.2.4 For all types of measurements considered, the interlaboratory deviation contributes the most important part to the total error. This has to be considered if efforts are made to improve the analytical performance and indicates the restricted value of increased numbers of repetitive analyses within the individual laboratory.

10.2.5 To facilitate and hasten sample transportation there is an urgent need to standardize container types and to simplify and normalize the administrative demands in the different countries.

10.2.6 The non-liquid spiking techniques (dry spike and aluminium-capsule method, use of metal alloy spike /Par. 8.4/) should be applied wherever possible because of their advantages concerning sample representativeness and stability as well as for facilitating transportation. However, the necessity to limit in-plant operation steps has to be considered.

10.2.7 Much attention has to be payed to correctness of transmitted data in respect to figures as well as to definition. If high numbers of similar numerical data have to be checked, the application of the Dixon criterion can be helpful to detect mistakes.

10.3 General

10.3.1 As the use of liquid sample material cannot be avoided completely, aging effects remain of importance at least for "chemically difficult" solutions. It seems recommendable, however, to study them on an academical basis within an individual laboratory rather than on a technological one.

10.3.2 As experiments of the IDA-72 type determine not only the actual "state of the art" of the method investigated but also improve it by helping the individual laboratories to recognize the weak points in their procedure, their continuation in future in this and/or other analytical fields seems very recommendable.

References

Volume I

/1/ F.H. Tingey, F.J. Balkovetz, D.M. Lund, J.E. Rein, F.W. Spraktes
and S.S. Yamamura
"Qualification of Umpire Laboratories for the Analysis of Uranium and Plutonium Materials Specifications", Idaho Nuclear Corporation, USAEC Contract AT (10-1)-1230 (May 1968)

/2/ Safeguard Analytical Laboratory Evaluation Program ("SALE"), performed on behalf of the USAEC
e.g. M.W. Lerner
"Safeguards Analytical Laboratory Evaluation (SALE) Study-Uranium Dioxide", New Brunswick Laboratory,
NBL-261 (1971)

S.S. Yamamura, F.W. Spraktes, G.J. Curtis, J.P. Clark, J.E. Delmore
"Observations on the Determination of Uranium By Isotope Dilution Mass Spectrometry", Allied Chemical Corporation, Idaho Falls,
not yet published

/3/ KFK 1100, EUR 4576e (1971)
Joint Integral Safeguards Experiment (JEX 70) at the EUROCHEMIC Reprocessing Plant, Mol, Belgium
Edited by R. Kraemer and W. Beyrich

/4/ R. Avenhaus
"Analysis of Variances"
see /3/,pp. 7-130

/5/ Kjeller Report KR-81 (1966)

Further References on Related Topics:

/6/ K.H. Neeb, W. Gebauhr
"Probleme der Kernbrennstoffanalyse"
Fortschritte der chemischen Forschung, 12 (1969), pp. 622-711

/7/ C. Beets
"Role of Measurements of Nuclear Materials in Safeguards"
BLG-490 (1974)

/8/ G.R. Waterbury [comp.]
"Analytical Methods for Fissionable Materials in the Nuclear Fuel Cycle". Program Status Report, June 1971-June 1972, LA-5064 (1972)

/9/ L. Koch
"Post-Irradiation Isotopic Analysis of Reactor Fuels"
B. Kaufmann [ed.]: Analytical Chemistry of Nuclear Fuels. Proceed. of a Panel on the ..., Org. in Vienna by the IAEA (13-17 July 1970). Vienna: Internat. Atomic Energy Agency 1972, pp. 111-118

/10/ J.E. Rein, C.F. Metz
"The Application of Isotope Dilution Mass Spectrometry to the Determination of Uranium and Plutonium in Nuclear Fuels".
see /9/, pp. 97-109

/11/ J.E. Rein, C.F. Metz
"The Determination of Nuclear Fuel Burn-Up Based on Isotope Dilution Mass Spectrometric Measurements"
see /9/, pp. 143-155

/12/ P.C. Puleio, C.E. Pietri, A.W. Wenzel, R.J. Greer, G.E. Peoples, A.W. Summers
"A Current Evaluation of the Isotope Dilution Mass Spectrometric Procedure for Determining Uranium and Plutonium"
NBL-265: C.D. Bingham: Annual Progress Report for the Period July 1971-June 1972 (1972),pp. 44-47

/13/ H.C. Jain, S.A. Chitambar, V.D. Kavimandan, G. Periaswamy, P.M. Shah, P.A. Ramasubramanian, C.K. Mathews, M.V. Ramaniah
"Mass Spectrometry"
BARC-690: R.H. Iyer, M.V. Ramaniah [eds]: Radiochemistry Division Annual Progress Report for 1972 (1973),pp. 30-33

/14/ J. Krtit
"Mass Spectrometric Determination of Uranium and Plutonium by the Isotope Dilution Method", Jaderna Energie, Vol. 19, No. 5 (1973), p. 121

/15/ J. Krtil [Czech]
"Hmotové spektrometrické stanovení uranu a plutonia metodou izotopového zředění" [Mass Spectrometric Determination of Uranium and Plutonium by the Isotope Dilution Method]
Jaderna Energie, Vol. 19, No. 4 (1973), pp. 121-124

/16/ "Bilan d'une comparaison interlaboratoires sur l'analyse du plutonium"
CEA-R-4364 (1972)

/17/ L.T. Hagie
"A Balanced Staggered Nested Design for the Estimation of Measurement Errors in Plutonium Determinations"
Nuclear Materials Management, 1, No. 3 (1972), pp. 155-160
CONF-720529: 13th Annual Meeting of the Institute of Nuclear Materials Management, Boston, MA., May 31-June 2, 1972

/18/ W. van der Eijk, R. Vaninbroukx
"Sampling and Dilution Problems in Radioactivity Measurements"
Nuclear Instruments and Methods, 102, No. 3 (1972), pp. 581-587
CONF-711002: 3rd Internat. Symp. on Research Materials for Nuclear Measurements, Oct. 5-8, 1971 Gatlinburg, Tenn.

/19/ K.F. Lauer, Y. Le Diugou
"Proper Use of Reference Materials for the Accurate Determination of Uranium, Plutonium and Thorium in the Nuclear Fuel Cycle"
M. Lewis [ed.]: Analytical Methods in the Nuclear Fuel Cycle. Proc. of a Symp. on ... held by the Internat. Atomic Energy Agency in Vienna, 29 Nov.-3 Dec. 1971. Vienna: Internat. Atomic Energy Agency 1972

/20/ A.von Baeckmann, J. Neuber, M. Wilhelmi, L. Koch
"Automatic Analysis of Uranium and Plutonium in Solutions"
see /19/, pp. 329-341

/21/ J.E. Rein, C.F. Metz
"Advantages and Limitations of Mass Spectrometry for the Measurement of the Isotopic Distributions of Uranium and Plutonium and Application to Nuclear Fuel Burn-Up"
see /9/, pp. 135-142

/22/ A.M. Moncassoli-Tosi, P.G. Rama, A.M. Bresesti, M. Bresesti, S. Facchetti, R. Klersy, F. Mannone, A. Schueremkaemper, A. Cricchio, L. Koch
"Post-Irradiation Burn-Up Analysis of Trino-Vercellese Reactor Fuel Elements. Comparison with Theoretical Results"
J.W. Weil /‾ed_7: Reactor Burn-Up Phyiscs. Proc. of a Panel on ..., Org. by the IAEA, Held in Vienna, 12-16 July 1971.
Vienna: Internat. Atomic Energy Agency 1973, pp. 197-225

/23/ A.J. Fudge
"A Review of Experimental Methods for the Determination of Nuclear Fuel Burn-Up"
see /22/, pp. 239-248

/24/ L. Koch et al.
"Uranium, Plutonium and Thorium Isotope Dilution Analyses for Irradiated Fuels", Progress Report 12, July 71-December 71, Transuranium Institute, Karlsruhe, Germany (1971)

/25/ D. Ertel, W. Wettstein
"Röntgenspektrometrische Simultanbestimmung von Uran und Plutonium in Lösungen bestrahlter Schnellbrüterbrennstoffe"
KFK 1121 (1970)