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The AS-76 Interlaboratory Experiment on the Alpha Spectrometric Determination of Pu-238

Part III: Preparation and Characterization of Samples

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Projekt Spaltstoffflußkontrolle

Kernforschungszentrum Karlsruhe

KERNFORSCHUNGSZENTRUM KARLSRUHE

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Abstract

Four plutonium samples containing 0.2, 0.8, 1.6 and 0.9 Atom % of ^{238}Pu have been prepared for the Interlaboratory Experiment AS-76. Of these, three were input solutions from a reprocessing plant. The fourth sample was from a plutonium product solution. These samples have been characterized by two alpha spectrometry laboratories and two mass spectrometry laboratories to certify the ratio of alpha activities $^{238}Pu/(^{239}Pu + ^{240}Pu)$ and the isotopic composition, respectively.

Zusammenfassung

Das Interlaborexperiment AS-76 zur alphaspektrometrischen Bestimmung von Pu-238

Teil III: Probenherstellung und Charakterisierung

Für das Interlaborexperiment AS-76 wurden vier Plutoniumproben hergestellt, die 0.2, 0.8, 1.6 beziehungsweise 0.9 Atom % ^{238}Pu enthielten. Drei dieser Proben stammten aus Eingangslösungen einer Wiederaufarbeitungsanlage. Die vierte Probe stammte aus einer Plutoniumproduktlösung. Diese Proben wurden durch zwei Alphaspektrometrie- und durch zwei Massenspektrometrie-Laboratorien charakterisiert, um einerseits das Verhältnis der Alphaaktivitäten $^{238}Pu/(^{239}Pu + ^{240}Pu)$ und andererseits die Isotopenzusammensetzung zu bestimmen.

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W. Beyrich and G. Spannagel

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Collection and Evaluation of Representative Spectra

G. Spannagel, W. Beyrich and G. Bortels*)

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Preface

The present report deals with the sample preparation for the AS-76 intercomparison and the characterization of the sample material. Since the alpha spectrometric assay was the exclusive subject of the intercomparison, explicit information on the procedure in use at those characterization laboratories has been included. The alpha spectrometric results, however, are an intermediate step in obtaining the isotopic ratio of $^{238}Pu/^{239}Pu$. For this reason, full attention has also been given to the question of the agreement between mass spectrometric and alpha spectrometric results.

It is felt that, when providing reference values in an intercomparison, a 3σ confidence level is quite appropriate. Therefore the accuracy of the results is expressed by means of their overall uncertainty, the random component of which is based on a 99.7 % (3σ) confidence level in case of a normal distribution. Not too strict an interpretation should be given to the exact figure of the actual confidence level since a straightforward statistical analysis had been performed.

The characterization values for the samples B, C and D are given in Chapter II.1. Sample A was found to be inhomogeneous, hence, no characterizations results are given for that sample.

The participating laboratories are the Atomic Energy Research Establishment, Harwell, the National Bureau of Standards, Washington, D.C., and the Central Bureau for Nuclear Measurements, Geel.

The authors express their appreciation to Paula Daems-Luypaerts, Roger Geeraerts, Juliaan Van Saene and Nicole Verboomen-du Bois de Nevele for their assistance in the preparation of the report and to the Kernforschungszentrum Karlsruhe for printing.

G. BORTELS.

Chapter I. SAMPLE PREPARATION FOR AS-76

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1. Introduction

The material from which the samples for AS-76 have been prepared at CBNM, Geel, was obtained from Kernforschungszentrum Karlsruhe (KfK). It consisted of two more dilute input solutions from a reprocessing plant, marked KRBII-27a and KRBII-22, respectively, and one undiluted plutonium product solution, marked 76/11-51. These solutions were received in plastic vials (Fig.I.1) which were sealed with a rubber septum and secured with a crimped aluminium cap. The solutions KRBII-27a and KRBII-22, in their vials without additional shielding, produced a (β,γ,x)-dose rate at 10 cm distance of 8 rad/h and 25 rad/h ★), respectively, due to fission products. The solution 76/11-51 was free from fission products and uranium.

Four new glove boxes have been installed and equipped for the sample preparation in order to eliminate risks of contamination. Each sample A, B and C has been prepared and sampled in a separate glove box; D and E were prepared and sampled in the same glove box. The three glove boxes for handling the γ-active solutions have been equipped with a small lead castle (Fig. I.2) in which the active solution was placed. This lead castle consisted of a few standard lead bricks machined to the correct size, covered with a 4 cm thick lead plate carrying a hole with slit for easy pipetting (Fig. I.3). Part of the glove box front was additionally shielded with lead foil and lead glass. The way the γ-active solutions KRBII-27a and KRBII-22, in the glove boxes, have been transferred from the vial into a glass bottle is shown in Fig. I.3. A sort of disposable collar was inserted in the bottle to prevent contaminating the bottle neck. The same protection was used later on for the glass vials when the aliquots were dispensed. The radiation dose accumulated on the fingers of the person working with the glove box was monitored with small radiothermoluminescence (RTL) dosimeters fixed onto the fingers. Work in the glove boxes was shared between four people; the absorbed dose on fingers when the entire sample preparation was finished was less than 0.6 rad. ★).

★) According to the EEC Directive 76/770/EEC /1/, the gray (Gy) is now the adopted unit of absorbed dose, replacing the rad: 1 rad = 10^{-2} Gy.

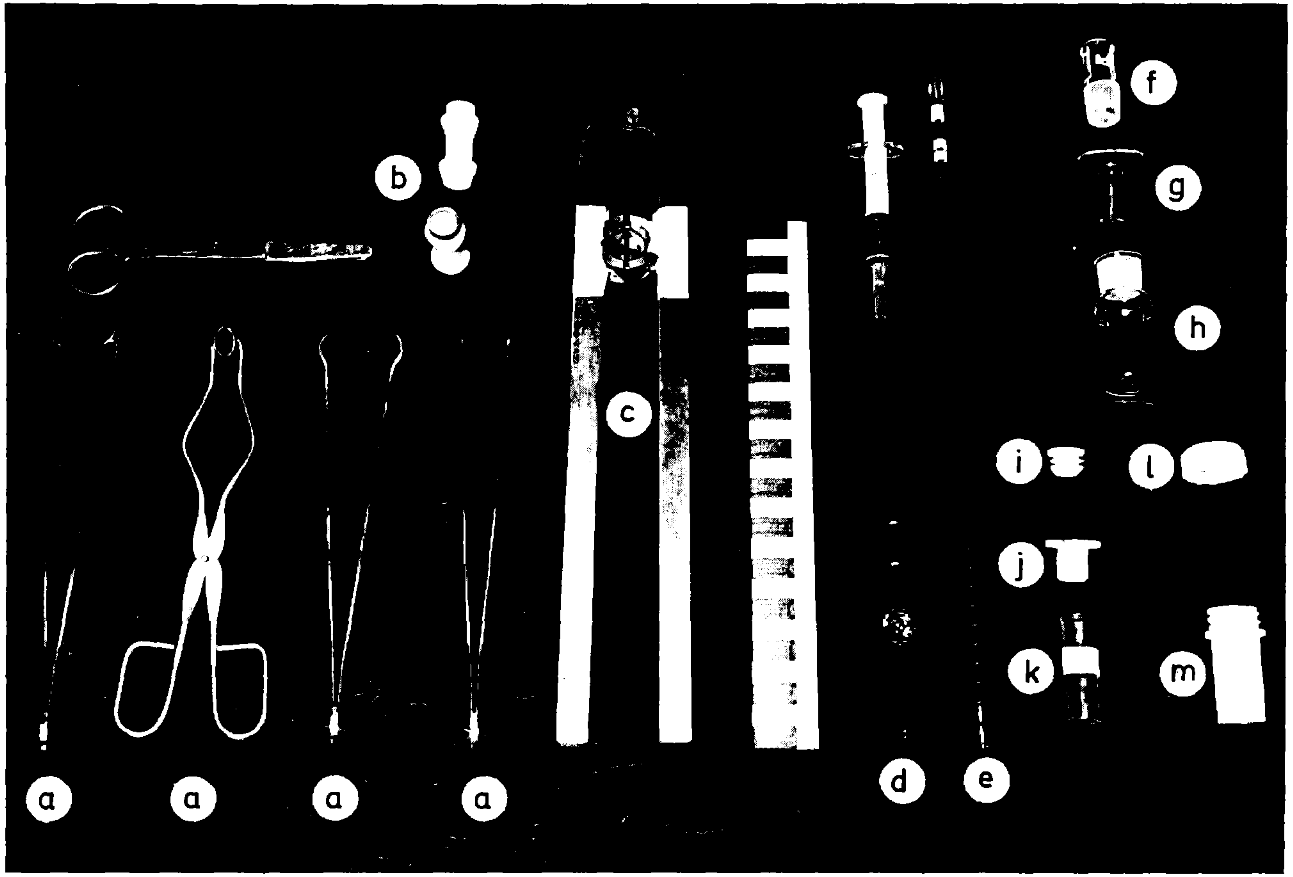


Figure I.1 a) Pincers and tweezers; b) Plastic vials used for shipment of the original solutions; c) Tool for opening the vials b; d,e) Glass pipettes; g,j) Disposable "collars" used to avoid contamination of the glass wall during pipetting; h,f) Glass bottle of 20 ml and stopper; k,i) Glass vial and stopper used for shipment of dry sample material to the AS-76 participants; m,l) Polytainer used for shipping dry sample material to AERE, Harwell.

Figure I.2 Equipment of glove box for handling AS-76 solutions containing fission products.

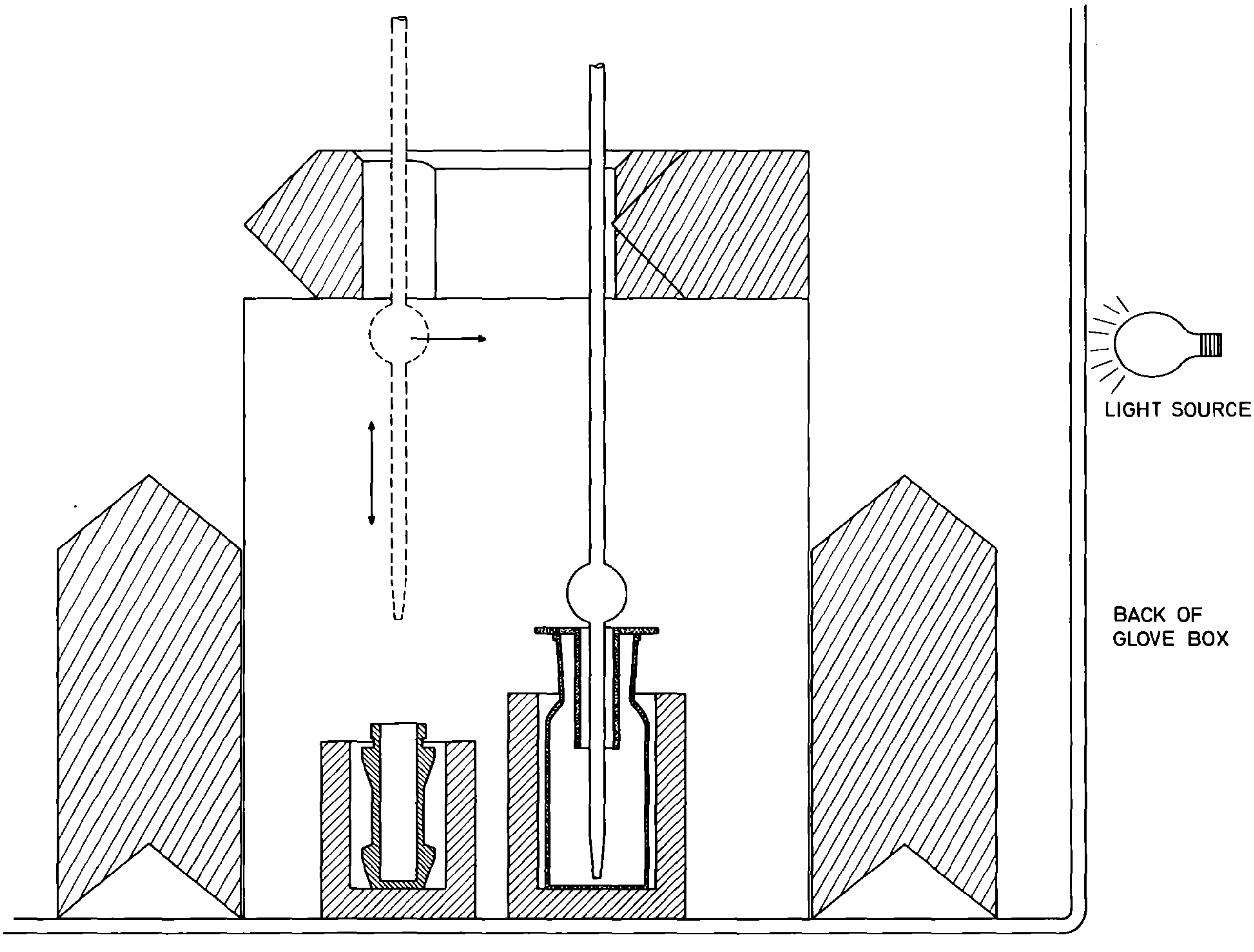
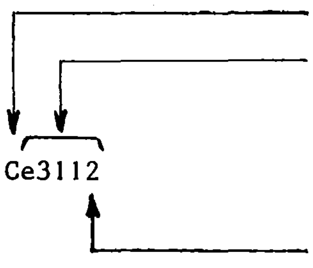


Figure I.3 Handling of AS-76 solutions containing fission products.

The different steps in the sample preparation are shown in the diagrams of Figs. I.4. to I.7. where the new glove boxes, numbered from 1 to 4, are also indicated.

Diagram blocks are labelled as follows:



Indicates the sample A, B, C, D or E

The preceding diagram block (parent solution) is found by omitting the last figure (2) and replacing the letter (e) by the preceding letter in alphabetical order, hence Cd311.

Numbering for different solutions from the same parent solution.

The specifications in the diagram blocks such as isotopic composition, concentrations, etc. refer to the situation after mixing. A heavy line at the left side of a diagram block indicates that the solution contains uranium and fission products. A double arrow means "the remainder of the solution".

The samples Ac33, Bc32 and Cc33 which were prepared for AERE, Harwell have been measured using RTL dosimeters to determine the (β,γ,x)-dose rates at a distance of 10 cm. All dose rates indicated in the sample preparation schemes were derived from these values. All samples dispatched to the different laboratories, either for assay or characterization, were sent as a dry residue. At least ten vials of each sample material were retained at CBNM as archive samples.

App. 1 gives some data of interest for the preparation of α-spectrometric sources. From the ^{241}Am ingrowth data it is clear that this correction is very small for sources measured within a reasonably short time after ^{241}Am separation. Some information on sample packaging is given in App. 7.

2. Samples A. (Fig. I.4.)

The solution KRBII-27a was delivered in three plastic vials of 3 ml each (b)[+)], labelled 1-8227.1, 1-8231.1 and 1-8233. The vials were put into glove box 2. From one of them, 2.4 ml of solution was transferred into a 20 ml glass bottle (h) (Aa) which was put into glove box 1. Amounts

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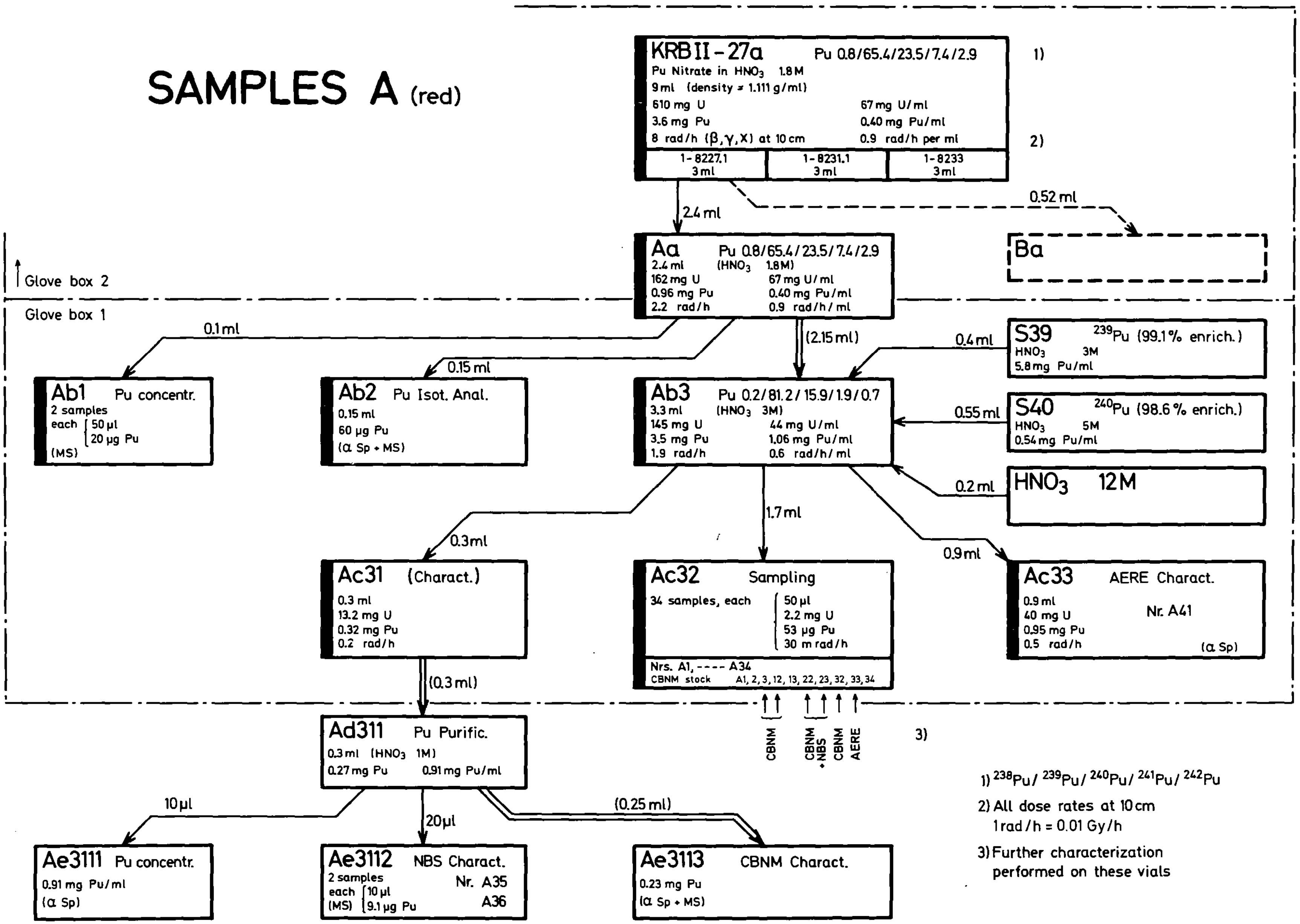
[+)] For underlined references (_), see Fig. I.1



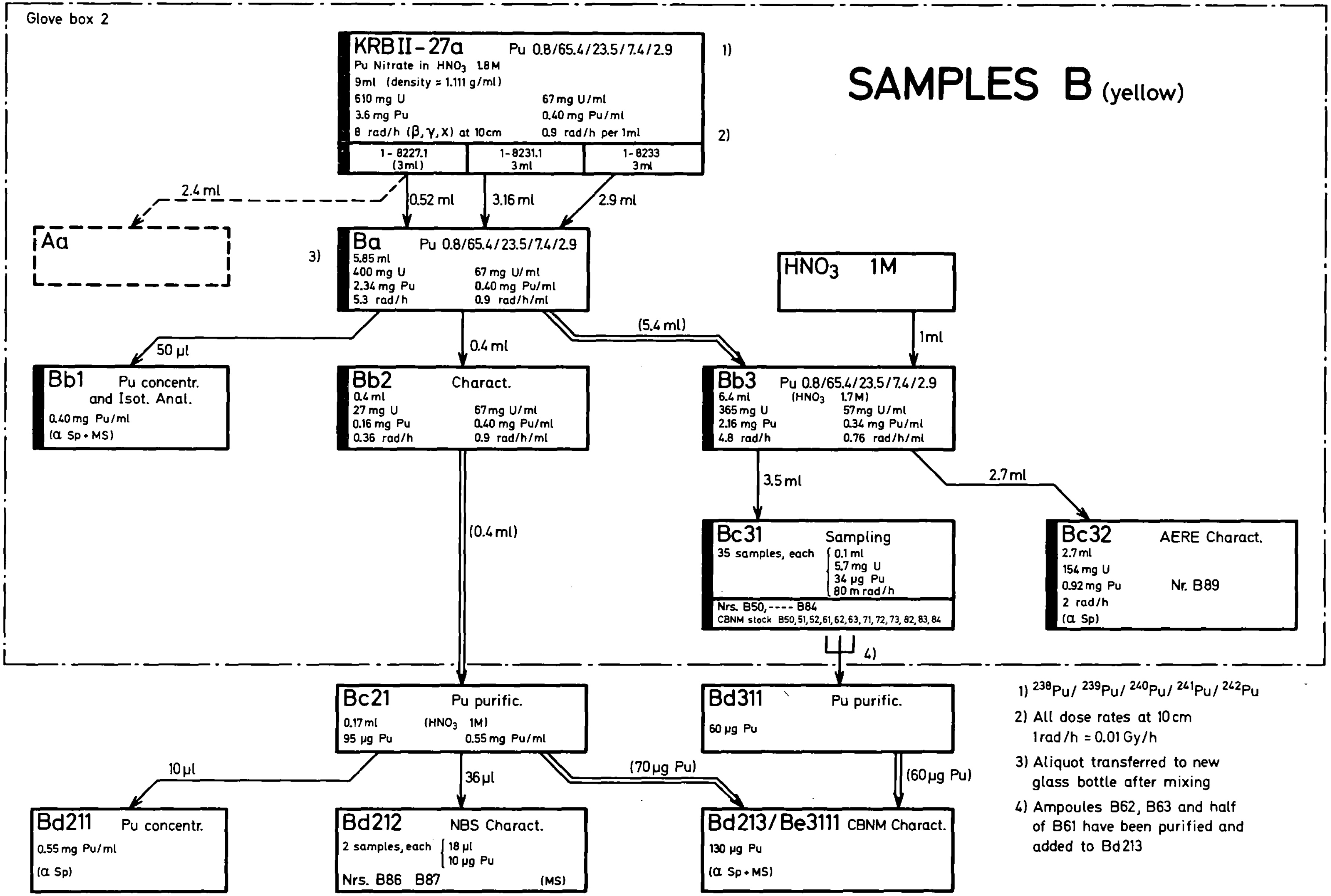
1) ^{238}Pu/ ^{239}Pu/ ^{240}Pu/ ^{241}Pu/ ^{242}Pu

2) All dose rates at 10 cm
1 rad/h = 0.01 Gy/h

3) Further characterization performed on these vials

A heavy line at the left side of a diagram block indicates that the solution contains U and fission products.
The double arrow means "the remainder of the solution".

Figure I.4 Preparation of samples A.



1) $^{238}Pu/^{239}Pu/^{240}Pu/^{241}Pu/^{242}Pu$

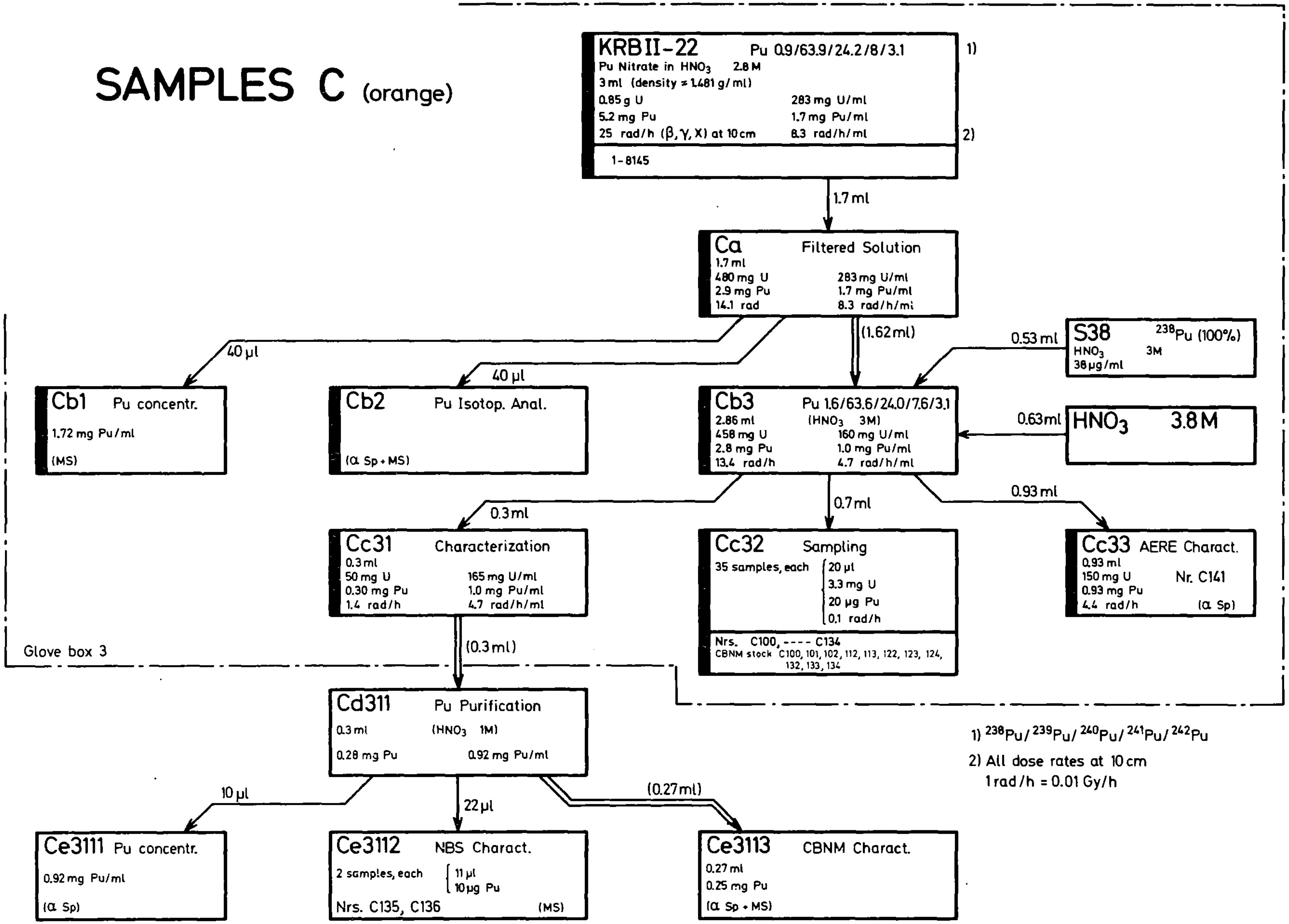
2) All dose rates at 10 cm
1 rad/h = 0.01 Gy/h

3) Aliquot transferred to new glass bottle after mixing

4) Ampoules B62, B63 and half of B61 have been purified and added to Bd213

A heavy line at the left side of a diagram block indicates that the solution contains U and fission products.
The double arrow means "the remainder of the solution".

Figure I.5 Preparation of samples B.

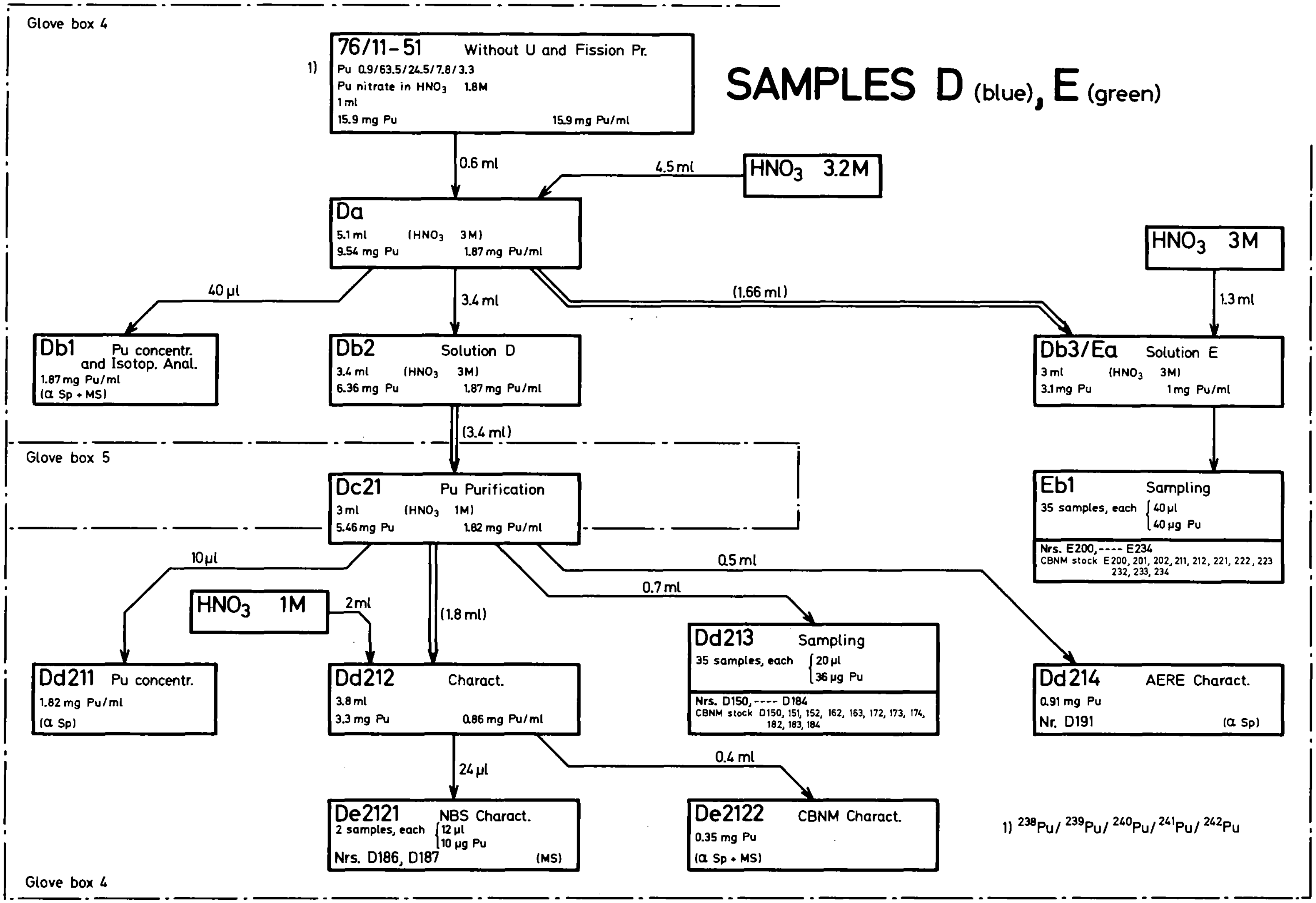


1) $^{238}Pu/^{239}Pu/^{240}Pu/^{241}Pu/^{242}Pu$

2) All dose rates at 10 cm
1 rad/h = 0.01 Gy/h

A heavy line at the left side of a diagram block indicates that the solution contains U and fission products.
The double arrow means "the remainder of the solution".

Figure I.6 Preparation of samples C.



The double arrow means "the remainder of the solution".

Figure I.7 Preparation of samples D and E.

Ab1 and Ab2 were then taken from Aa and analysed to determine the plutonium concentration and isotopic composition. The remainder of the solution Aa was spiked separately with ^{239}Pu and with ^{240}Pu from enriched solutions S39 and S40, respectively, using glass pipettes. Some nitric acid was added to bring the plutonium concentration in Ab3 at about 1 mg Pu/ml. The solution S39 was obtained from AERE, Harwell. The approximate concentration in S39 and S40 had previously been determined in a calibrated chamber for α-spectrometry at CBNM.

The solution Ab3 was shaken by hand for homogenization. On visual inspection it was a clear solution without residue. An aliquot of 0.3 ml was subsequently taken (Ac31) for the characterization at CBNM and NBS and transferred to a fume cupboard for plutonium separation. Next, 34 aliquots of 50 μl each (Ac32) were successively transferred from the solution Ab3 into glass vials (k) and evaporated to dryness. The vials were numbered from A1 to A34 and colour coded with a red mark. About 0.9 ml of solution Ab3 was subsequently transferred into a polytainer (m) (Ac33) using a glass pipette, evaporated to dryness and dispatched to AERE, Harwell for characterization.

The plutonium fraction obtained after a routine chemical treatment (Ad311) was made up with 1 molar nitric acid to obtain a concentration of approximately 0.9 mg Pu/ml. From the solution Ad311, two aliquots of 10 μl each were sampled (Ae3112) in separate glass vials (k), evaporated to dryness and labelled A35 and A36. These vials were for the characterization at NBS. The rest of the solution (Ae3113) was used for the characterization at CBNM.

3. Samples B. (Fig. I.5.)

These samples were prepared in glove box 2 from the solution KRBII-27a. An amount of 6.58 ml of solution was transferred from the three vials (b) into a 20 ml glass bottle (h) and shaken by hand for homogenization. From that solution, 5.85 ml was again removed with a glass pipette (d) and transferred into a similar 20 ml glass bottle Ba. On inspection, this solution was clear and free of residue. An amount Bb1 was analysed in order to be sure that the solutions contained in the three vials of KRBII-27a had the same origin. An aliquot of 0.4 ml (Bb2), which was intended for the characterization at CBNM and at NBS, was transferred to a fume cupboard for plutonium separation. Since about half the plutonium content of Bb2 was lost in a single plutonium purification run (Bc21), the vials B62, B63 and half of B61 were purified in Bd311 and added to Bd213. The samples for the characterization at NBS (Bd212) were evaporated to dryness and labelled B86 and B87.

Some nitric acid was added to the remainder of the solution Ba to obtain the solution Bb3 from which 35 aliquots of 0.1 ml each (Bc31) were successively transferred into glass vials (k) and evaporated to dryness. These vials were numbered from B50 to B84 and colour coded with a yellow dot. The solution Bb3 was subsequently transferred into a polytainer (m) (Bc32) using a glass pipette, evaporated to dryness and dispatched to AERE, Harwell.

4. Samples C. (Fig. I.6.)

The solution KRBII-22, which produced an absorbed dose rate of approximately 25 rad/h★) at a distance of 10 cm, was received in a 3 ml plastic vial (b). This vial was opened in glove box 3; about 2 ml of solution was removed with a glass pipette (d) and transferred into a 20 ml glass bottle (h). This solution contained a considerable amount of particulate matter which formed a black residue when the bottle was allowed to stand for a while. In order to remove the large particles, about 1.7 ml of the solution was put through a paper filter and collected in another 20 ml glass bottle (h) (Ca). On inspection, the filtered solution was clear. It is obvious that after filtering, the solution Ca became different from the original solution KRBII-22 but for the purpose of AS-76 this point is irrelevant.

Amounts Cb1 and Cb2 were analysed to obtain the plutonium concentration and isotopic composition. The remainder of the solution Ca was subsequently spiked with isotopically pure ^{238}Pu from the solution S38. Some nitric acid was added to bring the plutonium concentration of Cb3 at about 1 mg Pu/ml. The solution Cb3 was shaken for homogenization and sampled. About 0.3 ml was transferred into a glass vial (Cc31) for the characterization at CBNM and at NBS and taken to a fume cupboard for sepa-

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★) 25 rad/h = 0.25 Gy/h.

ration of the plutonium. Further, 35 aliquots of 20 μl each were successively transferred into glass vials (k) (Cc32) and evaporated to dryness. They were labelled from C100 to C134 and marked with an orange dot. Finally, for the characterization work at AERE, Harwell, 0.93 ml of the solution Cb3 was transferred into a polytainer (m) (Cc33) and evaporated to dryness.

The samples marked C135 and C136 were taken from the plutonium fraction Cd311 obtained after a single purification run. They were intended for the characterization at NBS. The remainder of the solution Cd311 which is marked Ce3113 in Fig. I.6. was further used for the characterization at CBNM.

5. Samples D and E. (Fig. I.7.)

The 1 ml undiluted plutonium product solution 76/11-51 from which the samples D and E were prepared was received in a 3 ml plastic vial (b). This solution did not contain uranium nor fission products and the plutonium concentration of about 16 mg Pu/ml is rather high. The samples D and E have been prepared in glove box 4 with the exception of the plutonium purification run (Dc21) which was carried out in a separate glove box 5. The glove box 5 was not a new box but had been reequipped and carefully checked to avoid contamination.

Approximately 0.6 ml of the solution 76/11-51 was transferred into a 20 ml glass bottle (h) and diluted with nitric acid to lower the plutonium concentration (Da). The plutonium concentration and isotopic composition were determined on sample Db1. About 3.4 ml of solution Da was transferred into a glass bottle (h)(Db2) to prepare the samples D. The solution Db2 was put into glove box 5 where it was purified in a routine chemical treatment (Dc21). The plutonium fraction Dc21 was transferred back to glove box 4 for further sampling. The approximate plutonium concentration of the solution Dc21 was measured on sample Dd211 by α-spectrometry in a known solid angle. From the purified solution Dc21, 35 aliquots of 20 μl each (Dd213) were successively transferred into glass vials (k), having a blue colour mark, and evaporated to dryness. They have been numbered from D150 to D184. About 0.5 ml of Dc21 was transferred into a polytainer (m) (Dd214) for characterization at AERE and evaporated to dryness. Some nitric acid was added to the remainder of the solution Dc21 for easier pipetting of the NBS samples. The resulting solution is indicated by Dd212 in Fig. I.7.

The solution E was prepared from the remainder of the solution Da after reducing the plutonium concentration to 1 mg Pu/ml. Again, 35 samples of 40 µl each were successively prepared and evaporated to dryness. The samples were numbered from E200 to E234 and marked with a green dot. Assay of the samples E was not part of the AS-76 intercomparison. If wanted, they allowed for doing some test analyses prior to starting the AS-76 intercomparison measurements.

6. Plutonium Purification

The plutonium purification procedure which was applied to all samples characterized at CBNM, to the samples D and to those which were sent to NBS, Washington, consists of a redox cycle followed by plutonium separation by anion exchange, according to a procedure used at SCK/CEN, Mol [★)].

The amounts of solution which are mentioned in the following description of the purification procedure apply to samples containing less than 25 mg of uranium and less than 0.5 mg of plutonium. The liquid sample was evaporated to dryness and the residue dissolved in 0.2 ml of 2M HNO_3. One drop of 1.25M $FeCl_2$ was added to the solution to convert the plutonium present to the III valent state. About 0.1 ml $NH_2OH.HCl$ 1M was subsequently added to stabilise the plutonium in the IV valent state into which it is converted by the addition of 0.1 ml $NaNO_2$ 1M. The solution was made up with about 0.43 ml of concentrated nitric acid to obtain a 8M HNO_3 sample ready for being transferred onto the anion exchange column.

The anion exchange column, having approximately 0.4 cm inner diameter, was loaded with DOWEX anion exchange resin 1x4 100-200 mesh to about 5 cm height. The column was washed with distilled water and conditioned with 8 molar nitric acid. The sample solution was loaded onto the column which was subsequently washed with 8M HNO_3 to remove ^{241}Am and fission products. The plutonium fraction was eluted from the column with 0.35M HNO_3, evaporated to dryness and redissolved in 1M HNO_3 to obtain a concen-

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[★] R. Boden and A.C. Demildt, SCK/CEN, Mol, Belgium; private communication.

tration of approximately 1 mg Pu/ml.

The sample Db2 (Fig. I.4.) which contained 6.36 mg plutonium was purified using a column with 0.8 cm inner diameter, loaded with the same type of anion exchange resin to about 10 cm height. About eight times larger quantities of chemicals were now used in that purification.

Chapter II. CHARACTERIZATION OF THE AS-76 SAMPLES

1. RESULTS OF THE CHARACTERIZATION OF THE AS-76 SAMPLES

G. Bortels, I.L. Barnes, P. De Bièvre, K.M. Glover

1.1 Introduction

The purpose of the characterization work for AS-76 is to certify on the reference date of 1st Nov. 1977, both the α-activity ratio $^{238}Pu/(^{239}Pu + ^{240}Pu)$ and the isotopic composition for the samples used. All samples have been prepared at CBNM, Geel.

The α-activity ratios have been determined by α-spectrometry at CBNM, Geel, and at AERE, Harwell. Both laboratories used their own routine techniques for sample purification, source preparation, measurement and spectrum analysis. Details of the α-spectrometric characterization work are given in the Secs. II.2 and II.3.

The atom ratios have been determined by mass spectrometry at NBS, Washington, and at CBNM, Geel, each laboratory using its own routine techniques. The samples used at NBS had previously been purified at CBNM in a single purification run. Details of the mass spectrometric characterization work are given in the Secs. II.4 and II.5.

It is the opinion of the characterization laboratories that final characterization values be deduced from the results of direct methods; that is, α-activity ratios from α-spectrometry measurements and isotopic compositions from mass spectrometry measurements. By so doing, additional uncertainties due to the use of combined half-lives are not included. Throughout Chapter II, the term "accuracy" is used exclusively to indicate an uncertainty for the mean value at the 99.7 % (3σ) confidence level as explained in App. 2.

1.2 Results of the Sample Characterization by Alpha Spectrometry

A number of parameters which are potential indicators of systematic errors have been investigated during the α-spectrometric measurements at AERE and at CBNM. Among them: the source preparation technique, the measuring equipment and the spectrum evaluation procedure. The two laboratories used their own chemical purification techniques except for the first plutonium separation of sample D which was carried out at CBNM. A large number of spectra having good counting statistics has been analysed. Finally, full attention has been given to detect impurity α-emitters as well as minor peaks belonging to the plutonium isotopes under investigation. The corrected results and their average values are given in Table II.1.1.

Table II.1.1 Results of the AS-76 Sample Characterization by α-Particle Spectrometry on Nov. 1, 1977

Sample	α-Activity Ratios ^{238}Pu/(^{239}Pu + ^{240}Pu) and Accuracies [x]		
	CBNM 1)	AERE 2)	Mean
B	1.4463 ± 0.0043 (0.30%)	1.4455 ± 0.0043 (0.30%)	1.446 ± 0.004 (0.30%)
C	2.984 ± 0.010 (0.35%)	2.9866 ± 0.009 (0.30%)	2.985 ± 0.010 (0.35%)
D	1.6361 ± 0.0057 (0.35%)	1.6382 ± 0.0050 (0.30%)	1.637 ± 0.006 (0.35%)

1) From Table II.2.4
2) From Table II.3.4

1.3 Results of the Sample Characterization by Mass Spectrometry

Thermal ionization mass spectrometry was used at NBS and at CBNM to measure the plutonium isotopic composition of the samples after three plutonium separations had been carried out on each of them. The materials investigated at NBS were plutonium fractions obtained after a first separation at CBNM. Strict and well established experimental procedures were applied by both laboratories, e.g. as to sample size, filament temperature, total ion current, sequence of measured ion ratios. In the case of the NBS results, the accuracies have been calculated from the values of the uncertainty for a single determination (95 % (2σ) confidence limit) on the base of a distribution of the results as in Fig. II.5.1. Table II.1.2 shows the corrected isotopic ratios and their accuracies. Table II.1.3 gives the mean values of the isotopic composition of the AS-76 samples B,C and D.

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[x] See App. 2 for the statement of accuracy.

Table II.1.2. Plutonium Isotopic Ratios in AS-76 Samples on 1st Nov. 1977 and Accuracies

Sample	NBS 1)				CBNM 2)			
	^{238}Pu/^{240}Pu	^{239}Pu/^{240}Pu	^{241}Pu/^{240}Pu	^{242}Pu/^{240}Pu	^{238}Pu/^{239}Pu	^{239}Pu/^{240}Pu	^{241}Pu/^{240}Pu	^{242}Pu/^{240}Pu
B	0.0337 ± 1.2 %	2.776 ± 0.15 %	0.3152 ± 0.15 %	0.1217 ± 0.25 %	0.0122 ± 0.8 %	2.776 ± 0.25 %	0.3152 ± 0.25 %	0.1216 ± 0.3 %
C	0.0687 ± 0.6 %	2.645 ± 0.15 %	0.3164 ± 0.15 %	0.1303 ± 0.25 %	0.0260 ± 0.7 %	2.646 ± 0.25 %	0.3159 ± 0.25 %	0.1298 ± 0.3 %
D	0.0370 ± 1.1 %	2.593 ± 0.15 %	0.3201 ± 0.15 %	0.1364 ± 0.25 %	0.0144 ± 0.8 %	2.593 ± 0.25 %	0.3197 ± 0.25 %	0.1362 ± 0.3 %

1) From Table II.4.1.
2) From Table II.5.3.

Table II.1.3. Mean Values of Isotopic Composition of AS-76 Samples on 1st Nov. 1977 (from NBS and CBNM Mass Spectrometric Measurements)

Sample	Atom %				
	^{238}Pu	^{239}Pu	^{240}Pu	^{241}Pu	^{242}Pu
B	0.80	65.37	23.55	7.42	2.86
C	1.65	63.59	24.04	7.60	3.12
D	0.91	63.46	24.47	7.83	3.33
(Mean values obtained from Tables II.4.2 and II.5.4)					

1.4 Comparison between Results of the $^{238}\mathrm{Pu}/^{239}\mathrm{Pu}$ Atom Ratios

The atom ratios of $^{238}\mathrm{Pu}/^{239}\mathrm{Pu}$, measured by mass spectrometry, are shown in Table II.1.4. These ratios can also be calculated from the ratios of α-activities $^{238}\mathrm{Pu}/(^{239}\mathrm{Pu} + {}^{240}\mathrm{Pu})$, measured by α-spectrometry, according to Eq. 1.

$$\left(\frac{^{238}\mathrm{Pu}}{^{239}\mathrm{Pu}}\right)_{(At)} = \left(\frac{^{238}\mathrm{Pu}}{^{239}\mathrm{Pu} + {}^{240}\mathrm{Pu}}\right)_{(\alpha)} \underbrace{T_{238}\left(\frac{1}{T_{239}} + \left(\frac{^{240}\mathrm{Pu}}{^{239}\mathrm{Pu}}\right)_{(At)} \frac{1}{T_{240}}\right)}_{K} \qquad (1)$$

In Eq. 1 the index (At) refers to an atom ratio; (α) indicates an activity ratio from α-spectrometric measurements, and the factor K contains the half-lives T_{238}, T_{239}, T_{240} of $^{238}\mathrm{Pu}$, $^{239}\mathrm{Pu}$, $^{240}\mathrm{Pu}$, respectively, and also the $^{240}\mathrm{Pu}/^{239}\mathrm{Pu}$ atom ratio from mass spectrometric measurements.

The value and accuracy of the factor K are calculated for the samples B, C and D using :

- mean values of $^{240}\mathrm{Pu}/^{239}\mathrm{Pu}$ and their accuracies obtained from the results of the mass spectrometric characterization, and
- half-lives of the isotopes involved, given in App. 3. The uncertainties of these half-lives, stated in App. 3, are 1/3 the accuracy; they were multiplied by a factor three, hence

$^{238}\mathrm{Pu}$ $T_{238} = (87.74 \pm 0.27)\,\mathrm{a}$
$^{239}\mathrm{Pu}$ $T_{239} = (24110 \pm 90)\,\mathrm{a}$
$^{240}\mathrm{Pu}$ $T_{240} = (6553 \pm 24)\,\mathrm{a}$.

Best values of the atom ratios and accuracies of $^{239}\mathrm{Pu}/^{240}\mathrm{Pu}$, obtained from the mass spectrometric measurements, are listed in Table II.1.5. The corresponding values for the atom ratio of $^{240}\mathrm{Pu}/^{239}\mathrm{Pu}$ are given in Table II.1.7.

In order to estimate the accuracy of K we have to consider the uncertainty contributions from the half-lives and from the measured atom ratio of $^{240}\mathrm{Pu}/^{239}\mathrm{Pu}$ which all have random and systematic components. Neither the degrees of freedom considered in the random components nor the relative importance of random and systematic components are well known. Therefore it seems reasonable to treat the uncertainty

Table II.1.4. Values and Accuracies of the Atom Ratios of ^{238}Pu/^{239}Pu in Samples B, C and D from different Characterization Laboratories and Methods.

Sample	Values and Accuracies of the Atom Ratios ^{238}Pu/^{239}Pu			
	From α-Spectrometric Measurements of Activity Ratios ^{238}Pu/(^{239}Pu + ^{240}Pu) 1)		From Mass Spectrometric Measurements	
			2)	3)
	C B N M	A E R E	N B S	C B N M
B	0.01224 ± 1.0 %	0.01223 ± 1.0 %	0.01212 ± 1.2 %	0.01221 ± 0.8 %
C	0.02596 ± 1.0 %	0.02598 ± 1.0 %	0.02598 ± 0.57%	0.02596 ± 0.7 %
D	0.01440 ± 1.0 %	0.01442 ± 1.0 %	0.01425 ± 1.1 %	0.01436 ± 0.8 %

1) Calculated using values of the activity ratios given in Table II.1.1, values of K from Table II.1.7, and using Eq. 1. The stated accuracy is the linear sum of the accuracies on the activity ratio and on the factor K.

2) The NBS values are calculated from the ratios of ^{238}Pu/^{240}Pu and ^{239}Pu/^{240}Pu given in Table II.4.1. The accuracy of the ^{238}Pu/^{239}Pu ratio is taken equal to the accuracy of the ^{238}Pu/^{240}Pu determination given in Table II.4.1.

3) Values and accuracies from Table II.5.3.

Table II.1.5. Values and Accuracies of Atom Ratios of ^{239}Pu/^{240}Pu

Sample	C B N M 1)	N B S 2)	Mean Value
B	2.7762 ± 0.0070 (0.25%)	2.7759 ± 0.0040 (0.15%)	2.7760 ± 0.0055
C	2.6458 ± 0.0070	2.6449 ± 0.0040	2.6453 ± 0.0055
D	2.5933 ± 0.0070	2.5929 ± 0.0040	2.5931 ± 0.0055

1) From Table II.5.3.

2) From Table II.4.1.

Table II.1.6. Contribution of different Parameters to the relative Accuracy of the Factor K in Eq. 1.

Parameter a_i	Δa_i	$\Delta K_i/K$ (%)
^{238}Pu half-life	0.27	0.31
^{239}Pu half-life	90	0.16
^{240}Pu half-life	24	0.21
^{240}Pu/^{239}Pu atom ratio	$8 \cdot 10^{-4}$	0.12
From linear sum (Eq.2) :	$\frac{\Delta K}{K}$ =	0.80 %
From quadratic sum (Eq.3) :	$\frac{\Delta K}{K}$ =	0.43 %

contribution from each parameter a_i of K as a systematic uncertainty which can either be combined by linear addition i.e.

$$\Delta K = \sum_i \left| \frac{\delta K}{\delta a_i} \Delta a_i \right| = \sum_i \left| \Delta K_i \right| \qquad (2)$$

or in quadrature i.e.

$$(\Delta K)^2 = \sum_i (\Delta K_i)^2 \qquad (3)$$

The uncertainty contribution ΔK_i from each parameter a_i was calculated (Table II.1.6) with Δa_i equal to the accuracy of the corresponding parameter. It is found that, in the case of the samples B, C and D, the influence from the ^{240}Pu/^{239}Pu ratio is rather small and that the other terms of $\Delta K_i/K$ have roughly the same magnitude.

Table II.1.7. shows the calculated values of the factor K. As four parameters contribute to the uncertainty of K and since their accuracies do contain both random and systematic components, in our opinion it is unrealistic to adopt the largest possible relative uncertainty (from Eq. 2). A rather conservative value of 0.7% has been adopted.

Table II.1.4 and Fig. II.1.1. show all results of the ^{238}Pu/^{239}Pu atom ratios of the samples B, C and D. The accuracy of 1.0 % for the α-spectrometric results is mainly due to the accuracy of the factor K. The results from α-spectrometric and mass spectrometric measurements (considering accuracies for the mean values and for a 99.7 % (3σ) confidence level) are in agreement with each other, although there seems to be a tendency for the mass spectrometric values to be lower than those from α-spectrometric measurements. This can not be due to a ^{238}U interference in the MS measurements. The results also suggest that the half-life values used are sufficiently accurate.

Table II.1.7 Values and Uncertainties of the Factor K of Eq. 1

Sample	Values and Accuracies of ^{240}Pu/^{239}Pu 1)	K 2)	$\frac{\Delta K}{K}$ (%) (Lin) 3)	$\frac{\Delta K}{K}$ (%) (Quadr) 4)	Adopted Accuracy of K (%)
B	0.36023 ± 0.00070	$8.4624 \cdot 10^{-3}$	0.8	0.4	0.7
C	0.37801 ± 0.00076	$8.7005 \cdot 10^{-3}$	0.8	0.4	0.7
D	0.38564 ± 0.00082	$8.8026 \cdot 10^{-3}$	0.8	0.4	0.7

1) From the mean values in Table II.1.5

2) See Eq. 1

3) From linear addition according to Eq. 2

4) From quadratic addition according to Eq. 3

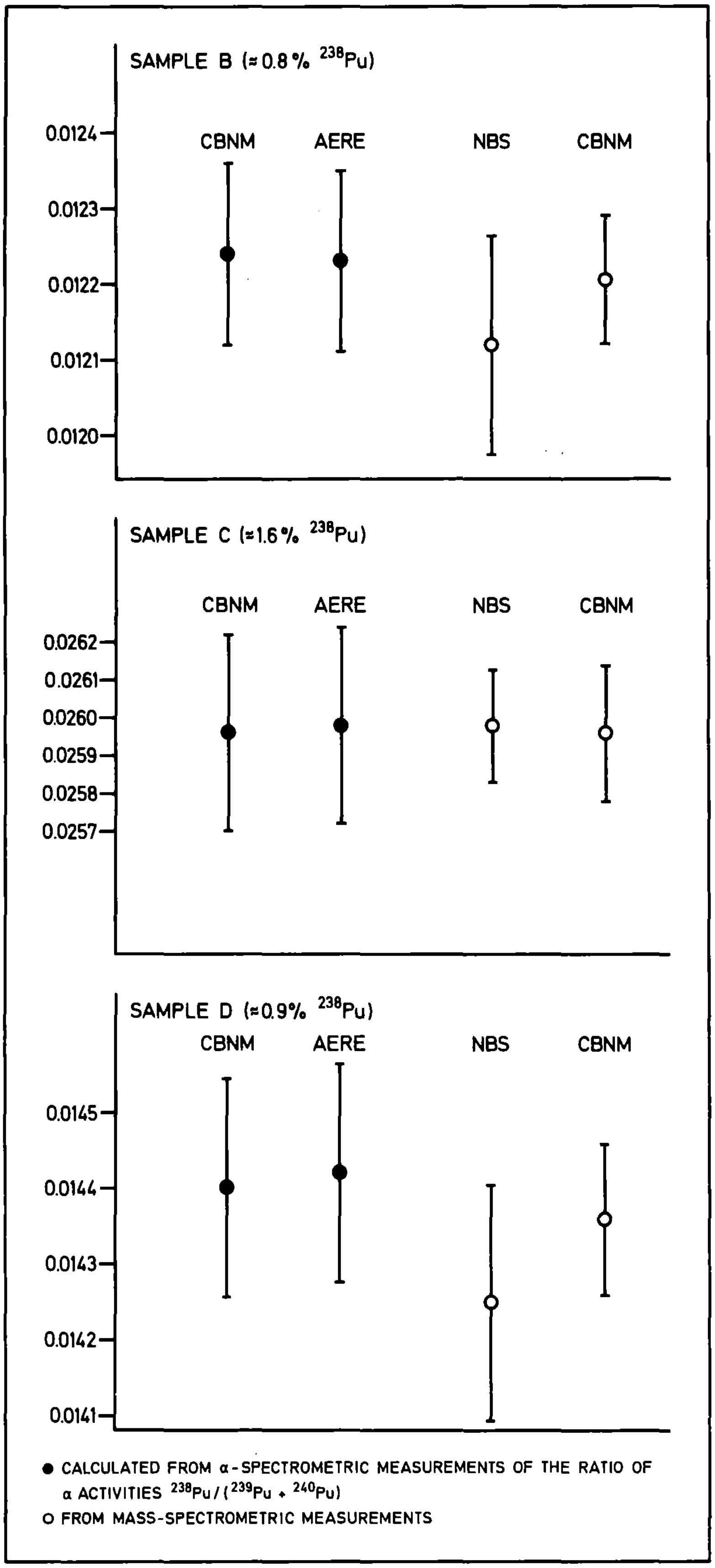

Fig. II.1.1 Atom ratios ^{238}Pu/^{239}Pu for AS-76 samples B, C and D. Error bars indicate the $\pm 3\sigma$ confidence interval and include an estimate of the systematic uncertainties.

1.5 Isotopic Inhomogeneity of Sample A

To prepare sample A, the total amount of plutonium in the original solution Aa (Fig. I.4) has been increased by a factor of four in order to reduce the ^{238}Pu concentration by the same factor. Sample A was found to be inhomogeneous with respect to plutonium isotopic composition, hence, no characterization values can be indicated.

A correlation between the ^{239}Pu/^{240}Pu atom ratios from mass spectrometry and the α-activity ratios ^{238}Pu/(^{239}Pu + ^{240}Pu) from α-spectrometry has been found and is shown in Fig. II.1.2. Here, results of measurements on a number of aliquots from the sample A are shown and a straight line has been drawn through the measurement points. The α-spectrometric results have been corrected towards the reference date. The result of the analysis of vial A33 is indicated by an arrow since the corresponding mass-spectrometric result is not available. The correlation found indicates the existence of different plutonium isotopic compositions which can be attributed neither to contamination nor to ingrowth of ^{241}Am nor to unsatisfactory characterization measurements.

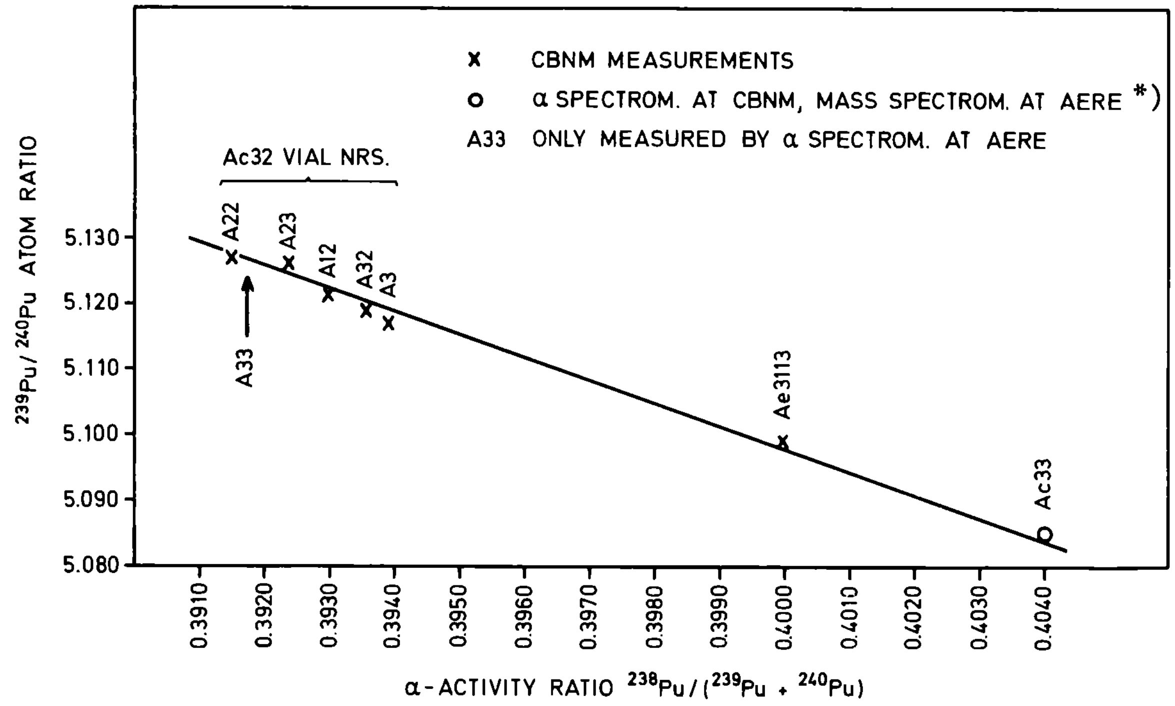

Figure II.1.2 Correlation between mass spectrometric and α-spectrometric results for different vials and solutions of sample A.

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*) E. Foster, AERE, Harwell, private Communication (Dec. 1978)

Since the spike materials were very low in ^{238}Pu concentration it is acceptable to assume that the amount of ^{238}Pu in the solution was not changed by the addition of ^{239}Pu and ^{240}Pu spikes. The Fig. II.1.2 then leads to the following conclusions:

i) among the vials examined, A22 shows the highest ^{239}Pu and ^{240}Pu concentrations,

ii) if lower concentrations of these isotopes are to be interpreted as a virtual loss of spike materials then one can deduce (App. 6) that the straight line corresponds to solutions for which approximately equal fractions of the ^{239}Pu and ^{240}Pu spikes are missing. This effect is not well understood since these spikes have been added separately. It is thought to be due to the behaviour of plutonium in solution containing particulate matter and polymers. More information about the measurements on sample A is given in Section II.2.5. An effect from suspended particulate matter on the concentration of plutonium in solution has recently been studied at KfK, Karlsruhe x).

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x) E. Mainka, KfK, Karlsruhe; private communication (Nov. 1978)

2. AS-76 CHARACTERIZATION BY ALPHA PARTICLE SPECTROMETRY AT CBNM, GEEL

G. Bortels
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2.1 Source Preparation

At CBNM the α-spectrometric measurements on samples A, B, C and D were performed on two types of sources:

- drop sources, with tetraethylene glycol (TEG) added as a spreading agent[x)], which were prepared at CBNM in the course of three successive identical chemical separations:
- sources evaporated in vacuum, prepared at AERE, Harwell, after a threefold purification of the sample material[+)].

All these sources were prepared on polished stainless steel trays of 27 mm diameter and 0.4 mm thickness.

Referring to the diagrams in Chapter I on sample preparation, the solutions from which the spectrometry sources were prepared are indicated in Table II.2.1.

Table II.2.1 Solutions used for the α-Spectrometric Characterization at CBNM

Sample	TEG spread sources		Sources evaporated in vacuum (prepared at AERE, Harwell)
	After first Pu purification	After 2nd and 3rd Pu purifications	
A	Ad311, Ac32	Ae3113	Ac33
B	Bc21	Bd213/Be3111	Bc32
C	Cd311	Ce3113	Cc33
D	Dc21	De2122	Dd214

In order to study the homogeneity of sample A additional sources have been prepared from five vials of the solution Ac32 which had been retained at CBNM as archive samples. These samples have only undergone a single purification run before the sources were made.

[x)] Preparation of tetraethylene glycol (TEG) spread sources is explained in App. 4.

[+)] See Sec. II.3

The chemical separations on all samples, except Dc21, were carried out in fume cupboards which are normally used for the assay of small safeguards samples. Great care was taken in cleaning and checking these cupboards and in handling the samples in order to avoid cross contamination. The TEG sources were prepared in a fume cupboard where similar precautions were taken.

The routine chemical treatment preceding the preparation of TEG sources consisted of a plutonium redox cycle followed by plutonium separation by anion exchange. This procedure is described in Section I.6. After the chemical separation, the plutonium fraction was evaporated to dryness and the residue dissolved in 1M HNO_3 to a concentration of approximately 1 mg Pu/ml. An aliquot of that solution, usually 5 µl or 10 µl, was taken using a glass disposable micro-sampling pipette. The solution was made up with 1M HNO_3 in order to obtain an α-disintegration rate per 10 µl of solution of between $10^4\ s^{-1}$ and $2 \cdot 10^4\ s^{-1}$. According to App. 1 these disintegration rates correspond to the following amounts of plutonium:

(2.2 - 4.4) µg Pu in the case of sample	A
(1.2 - 2.4) µg	B
(0.7 - 1.4) µg	C
(1.1 - 2.2) µg	D.

The α-spectrometry sources were subsequently prepared by dispensing 10 µl of solution on a polished stainless steel disc; a drop of a TEG solution was added and the sources treated as explained in App. 4.

The routine chemical treatment was applied three times to each of the samples A, B, C and D (except for the vials of the solution Ac32 already mentioned); usually one source was prepared after the first plutonium separation and three or four after both the second and third separation runs.

2.2 Data Acquisition

The spectrometry sources were counted in vacuum at 10^{-1}Pa - $5 \cdot 10^{-1}$Pa[x)]. A brass chamber of our own design, having a fixed source to detector distance of approximately 22 mm was used with three different Ortec silicon surface barrier detectors. The resulting source to detector

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[x)] The pascal (Pa) is the adopted unit of pressure: $1\ \text{torr} = \frac{101325}{760}$ Pa /1/.

geometry+) was determined versus a source of known α-disintegration rate. The geometries found were respectively:

0.35 % for a 25 mm^2 detector (premium grade),
1.3 % 100 mm^2 (" "),
1.7 % 150 mm^2 (ruggedized type).

All these detectors had 100 μm depletion depth.

The electronic equipment used consisted of: a Canberra preamplifier, model 970D, directly coupled to the detector via a Microdot-BNC connector; a Laben ADC, model 8215, giving 1024-channel to 8192-channel conversion gain (selectable); a Canberra spectroscopy amplifier, model 1413; a Canberra 8100 MCA (adapted to the Laben ADC) with 1024-channel memory; a detector bias supply, model 428 from Ortec; and a pulser of CBNM design.

Some count rate dependent spectrum deformation has been observed. This effect can easily be visualised at the pulser peak (Fig. II.2.1) where it tends to make the peak asymmetric by shifting its upper flank towards higher energy. Count rates have been maintained below 250 s^{-1} at which level spectrum deformation and pulse pile-up are negligible. The TEG sources and the vacuum evaporated sources were counted for a sufficient period of time to accumulate more than $5 \cdot 10^5$ counts and 10^6 counts, respectively, in the smaller of the two peaks (either the ^{238}Pu or the (^{239}Pu + ^{240}Pu) peak)). The spectra were recorded with 8192-channel conversion gain and stored in a 1024-channel memory covering the energy range 4650 keV - 5770 keV. The analyser output was punched on paper tape and read into the disk memory of the IBM 370/135 computer to list and plot the data and for analysing the spectra.

Most of the α-spectra were recorded using the 100 mm^2 detector. Spectrum resolution is primarily determined by the thickness of the active deposit of the source and to a lesser extent by the intrinsic resolution of the detector and by the noise of the electronics. Expressing the resolution in terms of the ratio of the 5499 keV peak height to the height of the ^{238}Pu tail (valley) at about 5200 keV, we found a figure of 600 to 3000 (typically 1000 to 1500) for the TEG sources and 4500 to 6000 for the sources evaporated in vacuum. The reason for the less reproducible

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+) The geometry is defined as the solid angle (steradian) /4π quality of the TEG sources is not known and the extreme figures were even obtained for sources from the same aliquot.

A search for α-emitting impurities in the samples was performed on three spectra recorded with 4096-channel conversion gain and stored in a 1024-channel memory, covering the energy range 4150 keV - 6300 keV; one TEG source of each sample B, C and D was counted for 10^7, $4 \cdot 10^6$ and $6 \cdot 10^6$ counts, respectively, in the smaller of the two peaks.
These spectra (Fig. II.2.1) show very weak peaks at about 4790 keV (possibly ^{237}Np) and at about 5710 keV and 5770 keV (possibly ^{236}Pu). They were all less than 0.01 % of the (^{239}Pu + ^{240}Pu) peak. The minor peaks at ≈ 5687 keV and at ≈ 6280 keV are unidentified. Several spectrometry sources were measured in a Si(Li) γ-spectrometer to look for possible incomplete ^{241}Am decontamination of the plutonium fraction at the time of chemical purification. No significant residual ^{241}Am was found.

2.3 Spectrum Analysis

The 1024-channel α-spectra from TEG sources have been analysed both by graphical interpretation and by computer. The spectra from the vacuum evaporated sources have been analysed by graphical interpretation only. Fig. II.2.2 shows a semi-log plot of a typical α-spectrum from a TEG source of sample C, counted with a 100 mm^2 detector at a count rate of 174 s^{-1}. With an ADC conversion range of 8K the 1K spectrum covers an energy range from about 4.7 MeV to 5.8 MeV.

Alpha-particle energies, relative intensities and half-live values for the isotopes of interest are found in App. 3.

Graphical Interpretation (Fig. II.2.2)

If the peaks are well resolved, the low energy tail below 4800 keV will show only a small slope. In the ideal case, when the tail below 4800 keV has almost settled to a constant value, the value for the ^{238}Pu tail contribution in that part of the spectrum is proportional to the ^{238}Pu α-activity, hence, the ratio A/B in Fig. II.2.2 is:

$$A/B = {}^{238}Pu \text{ α-activity/total Pu α-activity.}$$

The computer fits indicated that for medium to good quality TEG spectra, this ratio at about 4700 keV is well approximated by

$$A/B \approx 0.9\ {}^{238}Pu/({}^{239}Pu + {}^{240}Pu + {}^{238}Pu).$$

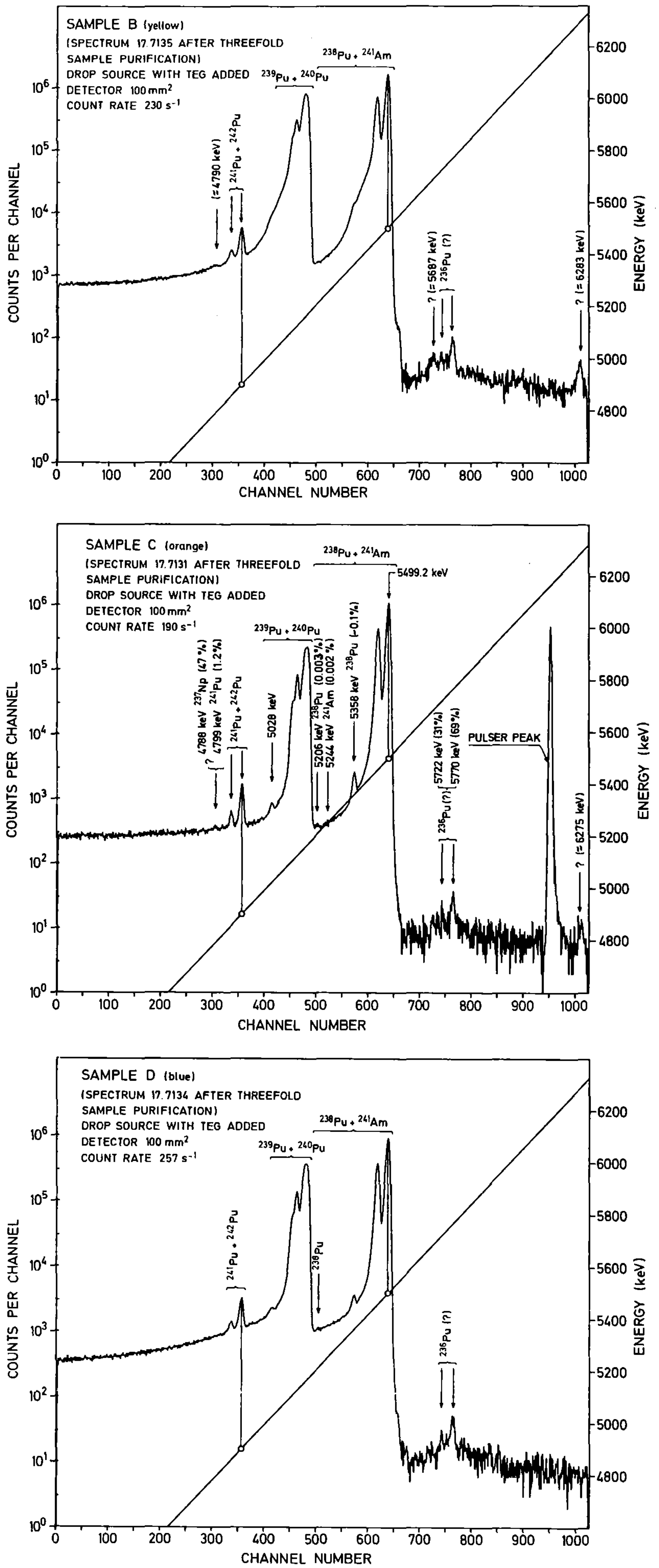

Figure II.2.1 Search for minor peaks from impurity α-emitting nuclides.

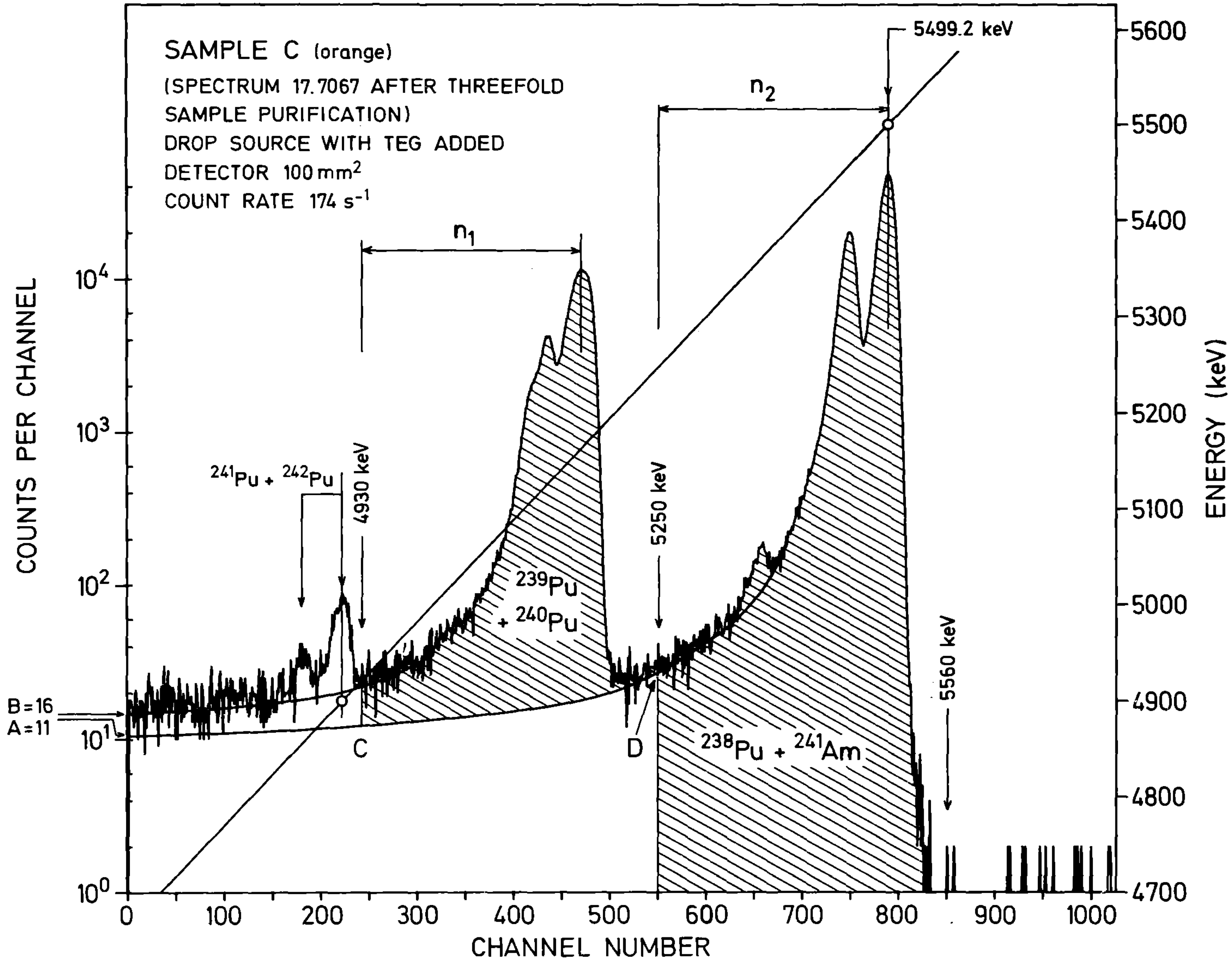

Figure II.2.2 Spectrum analysis by graphical interpretation.

The indicated ratio of isotopes is an α-activity ratio. The poorer the spectrum resolution, the lower the value for A/B. As a result, the point A (Fig. II.2.2) can easily be found with rather good precision and the tail attributed to the ^{238}Pu peak can be drawn.

The α-activity ratio ^{238}Pu/(^{239}Pu + ^{240}Pu) is determined from the number of counts in the respective peaks (shaded areas in Fig. II.2.2) considering appropriate energy intervals to these peaks. The size of these energy intervals is taken proportional to the energy of the major α-line in that interval, hence, in Fig. II.2.2 one has

$$n_1/n_2 \approx 5162/5499 = 0.939.$$

Here, 5162 keV is the mean value of 5155 keV and 5168 keV which are the energies of the major α-lines from ^{239}Pu and ^{240}Pu, respectively. In practice the point C is chosen arbitrarily at about 4930 keV which causes point D to be at about 5250 keV. The (^{239}Pu + ^{240}Pu) peak in the region (C,D) is corrected for ^{238}Pu tailing. This tail area is obtained from an integration applying Simpson's rule to a few points determined graphically on the ^{238}Pu tail in Fig. II.2.2.

The indicated graphical procedure performs well for spectra of good resolution, mainly because the strongest α-lines in the fine structure of these Pu isotopes are grouped in a somewhat similar way.

It is important to note (see also App. 3) that 99.98 % of the α-decays from ^{239}Pu and ^{240}Pu are emitted in the energy range 4930 keV - 5250 keV which is the energy range considered for the (^{239}Pu + ^{240}Pu) complex peak. Moreover, this energy range contains no α-lines due to ^{241}Am nor to ^{242}Pu but only 0.003 % of the ^{238}Pu α-decays and about 3 % of the ^{241}Pu α-decays. The energy range 5250 keV - 5560 keV which is considered for the ^{238}Pu peak accounts for 99.99 % of the α-decays from ^{238}Pu and ^{241}Am without any interference due to ^{239}Pu and ^{240}Pu. The energy range of roughly 4800 keV - 4950 keV covers more than 95 % of the α-decays from ^{241}Pu and ^{242}Pu.

Computer Analysis of the Spectra

Our actual computer code is an improved version of the one used in the ASET-74 intercomparison /2,3/. This code optimizes the tail of the ^{238}Pu peak by an iterative fit procedure based on an analytical expression for the shape of the fine structure peak arising from a single α-decay energy. In principle, it starts by decomposing the ^{238}Pu complex peak from which the shape parameters of the fine structure peaks are determined. In a further operation, these shape parameters were used to reconstruct the (^{239}Pu + ^{240}Pu) complex peak. The tail of that peak is calculated and compared with the tail in the pulse height spectrum near 4925 keV and below 4800 keV. The procedure is iterated until the calculated tail fits the spectrum tail. The programme uses data for the energies and relative intensities of the more important α-lines in ^{238}Pu (2 lines), ^{239}Pu (3 lines) and ^{240}Pu (2 lines) (App. 3).

As for the graphical interpretation, the α-activity ratio ^{238}Pu/(^{239}Pu + ^{240}Pu) is determined from the number of counts in the shaded peaks (Fig. II.2.2), but with two modifications:

- the correction for ^{238}Pu tailing in the region (C,D) is obtained from the fitted tail;
- a correction is applied to the shaded areas to consider equal energy intervals n_1 for all fine structure peaks in the (^{239}Pu + ^{240}Pu) complex peak, and n_2 for the two large single peaks in ^{238}Pu, respectively.

In both the graphical interpretation and the computer analysis, the number of counts in the ^{238}Pu peak was corrected for ^{241}Am ingrowth from the date of chemical separation to the date of counting (App. 1) and for ^{238}Pu decay to the reference date of 1st Nov. 1977. Background corrections ranging from zero to 0.023 s^{-1} in the ^{238}Pu peak have also been applied.

2.4 Results and Discussion

Table II.2.2 gives the essential information on our α-spectrometric results of samples B, C and D. Three α-activity ratios are indicated for each sample (columns I to III). For all three samples the lowest

TABLE II.2.2.

Details of α-Spectrometric Results at CBNM, Geel

		Sample B			Sample C			Sample D		
		Vac.☆) Graph. +)	TEG sources Graph. +)	Comp. o)	Vac. Graph.	TEG sources Graph.	Comp.	Vac. Graph.	TEG sources Graph.	Comp.
		I	II	III	I	II	III	I	II	III
Mean α-activity ratio ^{238}Pu/(^{239}Pu + ^{240}Pu)	$\overline{y}$	1.4454	1.4459	1.4485	2.9817	2.9830	2.9893	1.6342	1.6370	1.6390
Standard deviation of a single measurement	s(y)	0.0014 (0.10 %)	0.0022 (0.15 %)	0.0020 (0.14 %)	0.0032 (0.11 %)	0.0072 (0.24 %)	0.0057 (0.19 %)	0.0027 (0.16 %)	0.0044 (0.27 %)	0.0044 (0.27 %)
Standard error of the mean	s($\overline{y}$)	0.00037 (0.026%)	0.00057 (0.040%)	0.00052 (0.036%)	0.00090 (0.030%)	0.0015 (0.051%)	0.0014 (0.048%)	0.00078 (0.048%)	0.0010 (0.063%)	0.0010 (0.062%)
Number of sources counted		2	7	7	3	7	6	3	8	8
Number of pulse-height spectra		14	15	15	13	22	16	12	20	19
Correction to the (^{239}Pu + ^{240}Pu) peak due to underlaying ^{238}Pu tail (in % of the (^{239}Pu + ^{240}Pu) peak)		0.3-0.4	0.4-1.5	0.4-1.5	0.6-0.7	0.6-4.8	0.6-4.8	0.3-0.4	0.7-2.8	0.7-2.8
id. typical value		< 0.4	0.7	0.7	0.7	1	1	< 0.4	1.2	1.2
^{241}Am ingrowth correction to the ^{238}Pu peak (in % of that peak)		0.1-0.2	< 0.1	< 0.1	< 0.1	< 0.05	< 0.05	0.2	$\leqslant 0.1$	$\leqslant 0.1$

Remarks Indicated α-activity ratios are fully corrected and valid for 1 Nov. 1977. Since they are intermediate values, they have not been rounded off at this stage.

☆) Vacuum evaporated sources prepared at AERE, Harwell and measured at CBNM.
+) Spectrum analysis by graphical interpretation
o) id. by computer programme

activity ratio was obtained from the spectra of sources evaporated in vacuum. Next to it are the results from spectra of TEG sources analysed by graphical interpretation. The highest results were found for TEG source spectra analysed by computer. The number of purification runs was found to have no significant effect on the results from the TEG sources.

The results in columns I and II are statistically independent due to the very different source preparation techniques and chemical purification. They have been obtained by graphical interpretation of the measured spectra. If a modified t-test /4/ is applied to the results in the columns I and II it can be concluded that, for all three samples (although less conclusive for sample D), these results are not significantly different at the 95% confidence level. Hence, all the results in columns I and II can be considered to belong to the same population and can be pooled to give the results shown in Table II.2.3.

TABLE II.2.3.

Pooled Results from Graphical Interpretation only

		Sample B	Sample C	Sample D
Mean α-activity ratio	$\bar{y}$	1.4456	2.9825	1.6359
Standard deviation of single measurement *)	$S(y)$	0.0018 (0.13%)	0.0060 (0.20%)	0.0040 (0.25%)
Standard error of the mean *)	$S(\bar{y})$	0.00034 (0.024%)	0.0010 (0.034%)	0.00071 (0.044%)
Number of sources		9	10	11
Number of spectra		29	35	32
Random uncertainty (Student's $t_{(3\sigma)} \approx 3.3$)	$t_{(3\sigma)} \cdot S(\bar{y})$	0.024x3.3 = 0.08(%)	0.034x3.3 = 0.12(%)	0.044x3.3 = 0.15(%)

The results in columns II and III (Table II.2.2.) are not statistically independent since they arise from the same spectra analysed

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*) Sample estimates

by a different method only. They differ by 0.18 %, 0.21 % and 0.12 % for samples B, C and D, respectively. A modified t-test to these results indicates that they are significantly different for sample C but not for sample D. The test is not conclusive for the results of sample B. However, the results in columns I and III of samples B and D are significantly different. It is concluded that there is some indication of a small systematic uncertainty due to the method of spectrum evaluation, probably less than 0.2 %.

In our opinion the best results are obtained by taking the mean of the values in columns II and III and combining this value with the results in column I, hence according to (I+(II+III)/2)/2. These results are listed in Table II.2.4. Note that they differ by not more than 0.05 % from the results in Table II.2.3. The indicated accuracies[x)] consist of two components:

- a random component which is the standard error of the mean for a 99.7 % confidence level; it is the rounded value taken from Table II.2.3.
- estimated upper bounds to systematic uncertainties.

The stated accuracies cover all results given in columns I, II and III of Table II.2.2., including random uncertainties at the 99.7 % confidence level (calculated as $t_{(3\sigma)} \cdot S(\bar{y})$ with $t \doteq 3.3$ and $S(\bar{y})$ from Table II.2.2) to the highest and to the lowest values. A careful examination of the whole picture of values and their uncertainties justifies the assignment of an asymmetrical systematic uncertainty to the method of spectrum analysis. The uncertainty for residual ^{241}Am contamination at the time of purification indicated in Table II.2.4 is an upper limit.

Some uncertainty contributions were very small and have been neglected, e.g.

- α-lines from the decay of ^{238}Pu, ^{239}Pu and ^{240}Pu missing in the appropriate peak (Fig. II.2.2) or appearing in the other peak. As explained in Sec. II.2.3 the estimated influence on the α-activity ratio is approximately 0.03 %.
- α-emitting impurities in the sample, other than ^{241}Am. As explained in Sec. II.2.2 the very weak lines are fully negligible.

[x)] See App. 2.

TABLE II.2.4.

Best α-Activity Ratios and Accuracies from
CBNM Characterization

	B	C	D
Best α-activity ratio from CBNM determination $\bar{y}$	1.4463	2.984	1.6361
Accuracy	± 0.0043 (± 0.30 %)	± 0.010 (± 0.35%)	± 0.0057 (± 0.35 %)
Uncertainty Components (in % of activity ratio)			
Random uncertainty $t_{(3\sigma)} \cdot S(\bar{y})$ (for the mean and for a 99.7 % confidence level)	± 0.10	± 0.15	± 0.15
Systematic uncertainty from Σe			
- spectrum analysis	+ 0.20 - 0.10	+ 0.20 - 0.10	+ 0.20 - 0.10
- residual ^{241}Am after purification	+ 0.0 - 0.10	+ 0.0 - 0.10	+ 0.0 - 0.10
Accuracy	± 0.30	± 0.35	± 0.35

2.5. Characterization of Sample A

Referring to Chapter I, Fig. I.4., the solutions Ad311 and Ae3113 were characterized in the same way as all the other samples. The mean α-activity ratio obtained from TEG sources was 1.0% lower than our result from vacuum evaporated sources prepared at AERE, Harwell (solution Ac33). This difference was found to be significant. Additional sources were prepared from five of our archive vials of the material Ac32. All these vials were treated separately and with very much attention to detail in order to guarantee highly reliable results. The spread of the five α-spectrometric results was up to 0.64% which is not very conclusive on its own but these new results were up to 2.1% below the first TEG results (from Ae3113) and up to 3.2% lower than our results from the

Harwell sources. The correlation found (Fig. II.1.2) between the ^{239}Pu/^{240}Pu atom ratio from mass spectrometry at CBNM and our α-activity ratio ^{238}Pu/(^{239}Pu + ^{240}Pu) indicates that the different results are due to different Pu isotopic compositions, hence to inhomogeneity. It also highlights the reproducibility of the measurements. The effect is not due to a residual ^{241}Am contamination at the time of purification since this has been carefully checked by Si(Li) γ-spectrometry. Contamination can also be excluded as a possible explanation since all equipment and solutions used were fully checked.

2.6 Conclusions

Drop deposition sources with tetraethylene glycol added as a spreading agent and sources evaporated in vacuum (prepared at AERE, Harwell) have been measured at CBNM to determine the α-activity ratio ^{238}Pu/(^{239}Pu + ^{240}Pu) for the AS-76 samples A, B, C and D. Results for the samples B, C and D are given in Table II.2.4.

The characterization of sample A was unsuccessful due it is thought to inhomogeneity with respect to the plutonium isotopes. The reason for this is not known but an effect from particulate matter and polymers cannot be excluded. Such effects could be important when plutonium spiking techniques are used.

Acknowledgement

The work of R. Vaninbroukx, who checked the ^{241}Am content of the sources by γ-spectrometry, and of W. Zehner, who assisted in part of the source preparation, is gratefully acknowledged.

3. AS-76 CHARACTERIZATION PROCEDURES CARRIED OUT AT AERE HARWELL

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3.1 Chemical Separation

Identical chemical separation procedures were applied to each of the samples A41, A33, B89, C141, D191 x) supplied to Harwell for characterization. Great care was taken in handling these samples. A clean completely re-equipped and redecorated laboratory suite was used for chemical processing, to eliminate the possibility of contaminating the samples. To avoid cross contamination between samples, each sample was processed separately in a clean fume cupboard using new apparatus.

The samples were dissolved in 2 ml 8M HCl containing 0.1M HNO_3, to convert the plutonium present in solution to the IV valent state. Approximately 0.5 ml of each sample were retained as archive samples. The plutonium was separated from the americium, uranium, neptunium and fission products present, by anion exchange. Columns approximately 8 cm x 0.5 cm loaded with BIORAD anion exchange resin AG1 - X4 100-200 mesh, 1.2meq/ml of resin bed and conditioned with 8M HCl, were used. A new column and equipment were used for each anion exchange separation.

In each case the sample solution was loaded on to the column which was then thoroughly washed with 8M HCl to remove ^{241}Am and the majority of the fission products. Occasionally some breakthrough of plutonium in III valent state occurred at this stage. The plutonium fraction was eluted with 8M HCl containing 0.05M NH_4I and finally the neptunium and uranium were eluted from the column by washing with 0.25M HCl. The plutonium solution was reduced to dryness and concentrated nitric acid was added to remove the iodine, this step was repeated twice and finally the plutonium fraction was redissolved in 8M HCl containing 0.1M HNO_3 in preparation for the second anion exchange run. This procedure was repeated for the third and final anion exchange column run carried out on each sample immediately prior to source preparation to ensure complete removal of ^{241}Am. The date and time of the final plutonium separation were noted for each sample.

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x) See Chapter I, Fig. I.4 to I.7

3.2 Source Preparation

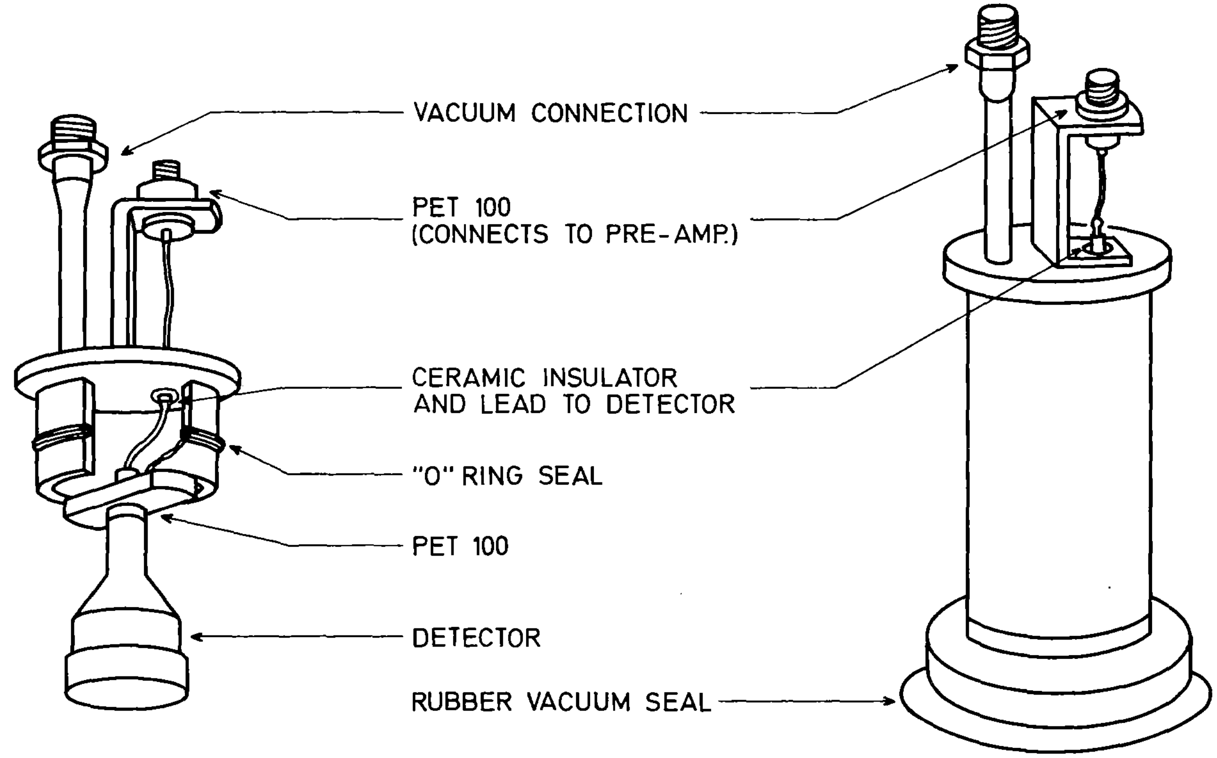
The sources for the alpha spectrometry measurements were in each case prepared from the plutonium fraction of the third anion exchange column. This fraction which was taken down to dryness and finally redissolved in 2M HCl. The solution was concentrated to give an α-activity of approximately 2.5 x 10^5 Bq/5μl. The sources for characterization were prepared by two techniques, vacuum evaporation and a spreading technique using tetraethylene glycol (TEG) as a spreading agent. These two techniques are described in App. 4 and 5.

All the sources characterized at Harwell except those from A33, were prepared by vacuum evaporation on to 27 mm diameter polished stainless steel substrates. Source strengths of approximately $1.6 \cdot 10^4$ Bq were deposited over 7 mm active diameter at the centre of the stainless steel backing discs. In order to eliminate cross contamination between samples, clean vacuum evaporation equipment was used for each of the samples A41, A33, B89, C141 and D191.

Eight sources were prepared from the purified plutonium fraction obtained from each of the samples, A41, A33, B89, C141 and D191. Three sources from each sample were sent to CBNM, Geel, for analysis. The remaining sources were analysed at Harwell.

3.3 Data Acquisition

The sources were analysed using a pair of Ortec 25 mm^2 surface barrier detectors each mounted in a chamber designed by the alpha spectrometry section at Harwell, (shown in Fig. II.3.1.). One of the surface barrier detectors was connected to an Intertechnique Didac 800 channel analyser through a pair of Ortec amplifiers type 124 and 471 and the other was similarly connected to another Didac 800 analyser through a pair of Harwell amplifiers type 0351 and 2151. The Didacs numbered 1 and 2 were each set at 5 mV channel width. The counts from the sources were stored in 400 channels of each analyser and the respective backgrounds were stored in the remaining 400 channels. A background correction was applied to each source scan. To optimise resolution and counting duration and to avoid the use of a pulse pile up rejection system, the source to detector distance was adjusted to give a count rate of less than 200 s^{-1}.



TOP AND DETECTOR

COMPLETE ASSEMBLY

Figure II.3.1 A new surface barrier detector chamber for in situ contamination identification.

At the same time a source to detector distance of greater than 1 cm was maintained such that the solid angle subtended by the source at the detector was sufficiently low to eliminate scattered alpha particles and to ensure that alpha particles of the same energy had nearly equal track lengths in the detector. The geometry under these conditions was roughly 2 % determined against a standard source previously measured in a low geometry counter. The geometry was measured for each surface barrier detector and maintained constant during all the measurements. Each source was counted for a sufficient period of time to accumulate 10^6 counts in the smaller peak. The vacuum in the chambers was maintained at 10^{-2} Pa x).

All the sources prepared from each of the samples were analysed three times in each surface barrier detector chamber giving a total of six scans per source. An energy calibration was carried out for each spectrum. The backgrounds were continually updated during the characterization measurements.

3.4 Data Evaluation

Linear plots of all the spectra recorded were hand plotted. Fig. II.3.2 shows a spectrum from D191 as received. Fig. II.3.3 shows a typical spectrum recorded on D191 source 7. For the evaluation of all the sources characterized at Harwell further spectra were hand plotted using an expanded scale for the Y axis to enable accurate interpretation of the low energy tails and the low abundance isotopes ^{241}Pu and ^{242}Pu. This expanded scale also highlighted the fine structure of the major plutonium isotopes. Fig. II.3.4 shows the expanded spectrum of source 7 D191 analysed on Didac 1.

The low energy tails of the (^{239}Pu + ^{240}Pu) and the ^{238}Pu peaks were evaluated by graphical interpretation. The low energy tail of the (^{239}Pu + ^{240}Pu) complex was plotted as a best fit through randomly distributed points. The ^{238}Pu low energy tail was plotted by analogy with the (^{239}Pu + ^{240}Pu) low energy tail. The activity of the ^{238}Pu peak as a percentage of total alpha obtained by integrating the areas under the peaks without any tailing corrections was used to confirm that the intercept of the ^{238}Pu tail with the Y axis had been plotted correctly. This

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x) 1 torr = $\frac{101325}{760}$ Pa /1/.

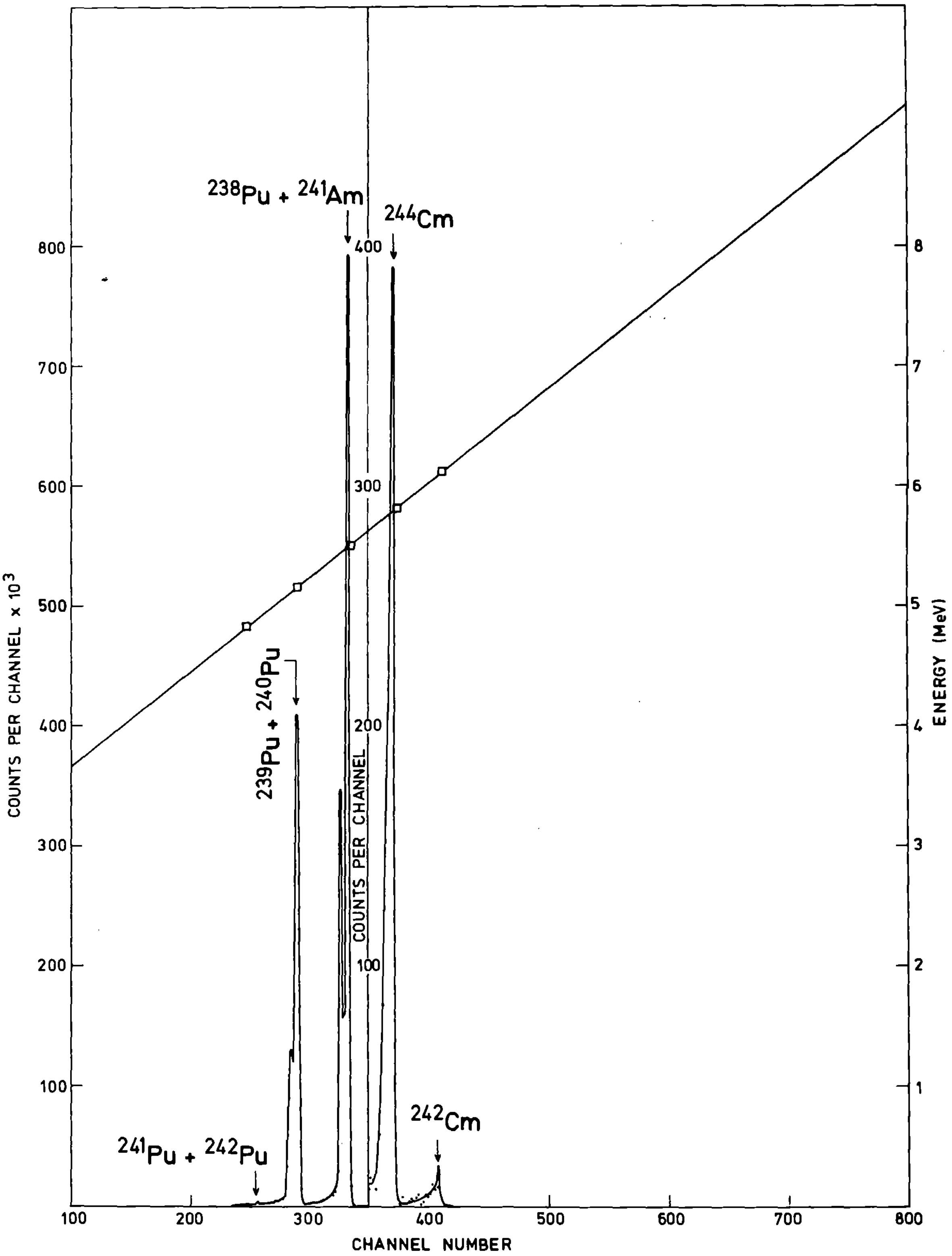

Figure II.3.2 Alpha-particle spectrum from the material in vial D191 as received.

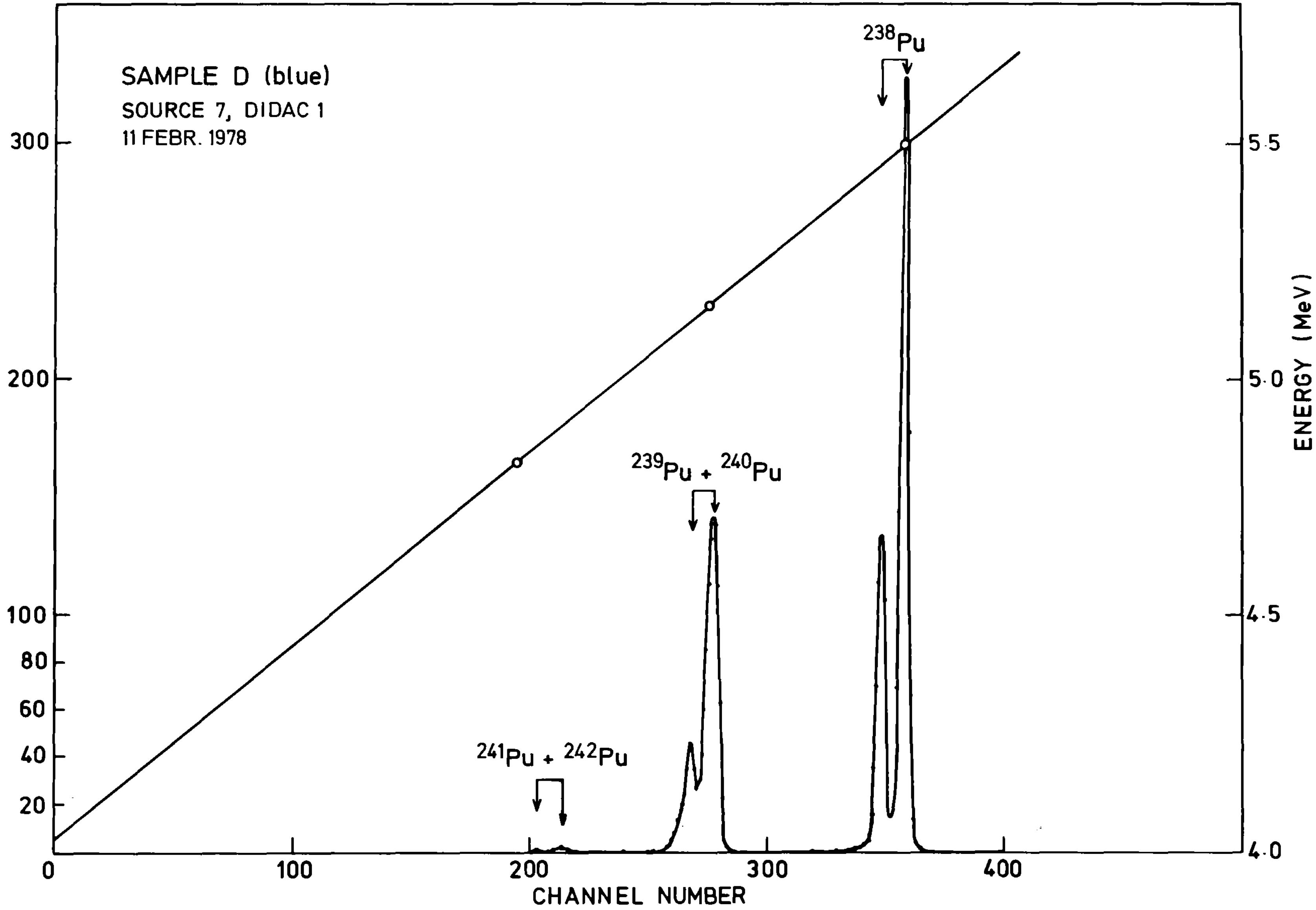

Figure II.3.3 Typical α-particle spectrum from the plutonium fraction of sample D191.

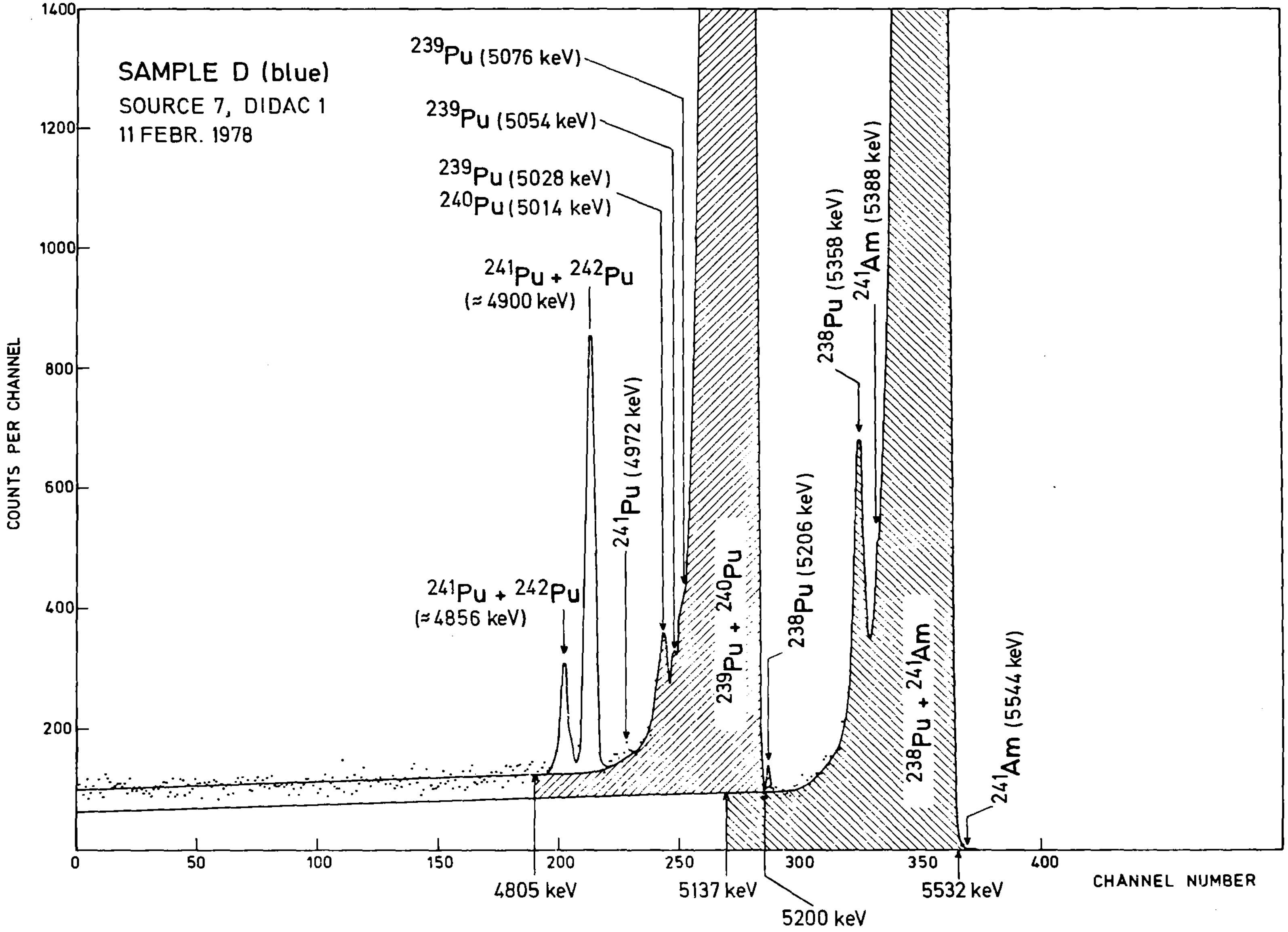

Figure II.3.4 High resolution α-particle spectrum from a separated plutonium fraction. (Source obtained by evaporation in vacuum).

intercept is porportional to the activity of the peak under consideration.

If one considers that the low energy tail below 4800 keV exerts no significant influence on the final result, corrections need only be applied in the region 4800 keV - 5500 keV. Any ^{237}Np present in the solutions as received would have been separated in the anion exchange purification steps and any significant quantities of ^{237}Np remaining in the samples would have been detected in the alpha spectra. The alpha particle energies and half lives relevant to the evaluation are listed in App. 3.

The ^{238}Pu peak was evaluated in the energy range 5137 keV - 5532 keV (395 keV), which included all the alpha lines due to ^{238}Pu. The counts due to the ^{238}Pu tail were interpreted from the graph and included with the ^{238}Pu peak. The (^{239}Pu + ^{240}Pu) peak was evaluated over the energy range 4805 keV - 5200 keV (395 keV) which included all lines due to ^{239}Pu, ^{240}Pu, ^{242}Pu and all lines due to ^{241}Pu except 4799 keV and 4784 keV. The contribution to the (^{239}Pu + ^{240}Pu) peak from the ^{241}Pu and ^{242}Pu peaks was calculated by applying corrections to the analyser data, which were read from the graph. The correction to be applied to the (^{239}Pu + ^{240}Pu) peak for the contribution from the ^{238}Pu tail was evaluated from the graph. In Fig. II.3.4. shading indicates the areas evaluated to obtain the activity ratio $^{238}Pu/(^{239}Pu + ^{240}Pu)$.

The ^{238}Pu peak was corrected for the growth of ^{241}Am from the date of the final column separation to the analysis date. Similarly a correction was made for the decay of ^{238}Pu to the reference date November 1st. 1977. Half lives used are listed in App. 3.

In the graphical evaluation of a linear plot spectrum, errors can be introduced by the incorrect assignment of ^{238}Pu, (^{239}Pu + ^{240}Pu), ^{241}Pu and ^{242}Pu counts from one evaluation to the next, from one evaluator to another and between evaluation techniques. In addition to the statistical counting error, a systematic instrumental error may also be introduced. However assuming that the solution is homogeneous and that reliable equipment is used, the overiding factor influencing the accuracy of the result obtained is the quality of the source itself.

The sources prepared and characterized at Harwell, were analysed in two separate sets of equipment. Two Ortec silicon surface barrier detectors were used whose performance was not identical. One detector was used in conjunction with Harwell amplifiers and the other with Ortec amplifiers. The output pulses from both systems were fed into Intertechnique Didac 800 channel analysers, Didac 1 and Didac 2. Typical peak to valley ratios for the ^{238}Pu peak measured from 5499 keV to 5250 keV and for the (^{239}Pu + ^{240}Pu) peak measured from 5162 keV to 4800 keV are shown in Table II.3.1. together with typical resolution values measured in keV at full width half maximum peak height (FWHM).

Table II.3.1. Typical Peak to Valley and Resolution Values

Analyser	^{238}Pu peak/valley	(^{239}Pu+^{240}Pu) peak/valley	^{238}Pu Resolution keV FWHM	(^{239}Pu+^{240}Pu) Resolution keV FWHM
Didac 1	3900/1	1300/1	16	24
Didac 2	2262/1	840/1	18.5	27.7

An assessment of systematic instrumental uncertainties was made by evaluating separately the data from each sample for the two sets of equipment and comparing the results. In addition some spectra were evaluated over the energy range 5532 keV - 4880 keV without applying any correction for the ^{238}Pu tail and comparing the values with those obtained from the spectra evaluated by the standard technique over the energy range 5532 keV - 4805 keV. These results are shown in Table II.3.2.
To make an assessment of the evaluator uncertainties, some spectra were interpreted by two evaluators A and B. These results are compared in Table II.3.3.

To minimise radiation dose to personnel, fission products and trivalent actinides were removed before any analyses were made on the initial solutions A41, B89 and C141. However TEG spread sources were prepared from solutions D191 and A33 as received and alpha spectrometry measurements were made. The ^{242}Cm and ^{244}Cm peaks were measured on these samples and the contributions to the ^{238}Pu and (^{239}Pu + ^{240}Pu) activities on the reference date November 1st 1977 was calculated from the decay of these two nuclides respectively. For solution D191 the activity ratio ^{244}Cm/(^{239}Pu + ^{240}Pu) was 0.001 and the activity ratio ^{242}Cm/^{238}Pu was 0.0003. For solution A33 the corresponding values for the activity ratios ^{244}Cm/(^{239}Pu + ^{240}Pu) and ^{242}Cm/^{238}Pu were found to be 0.13 and 0.005.

Table II.3.2. Comparison of Results from different Evaluation Methods and Instruments

Sample Data	Didac 1			Didac 2		
	Mean Value	σ 1)	n 2)	Mean Value	σ 1)	n 2)
Yellow B89						
Energy Range 5.53 - 4.80 MeV normal evaluation	1.4450	0.0015	10	1.4460	0.0023	11
Energy Range 5.53 - 4.88 MeV without tailing correction	1.4447	0.0015	6	1.4455	0.0028	5
Orange C141						
Energy Range 5.53 - 4.80 MeV normal evaluation	2.9869	0.0028	10	2.9863	0.0039	12
Blue D191						
Energy Range 5.53 - 4.80 MeV normal evaluation	1.6382	0.0029	8	1.6381	0.0019	8

1) Standard deviation of single measurement, based on the stated number of measurements.

2) Number of measurements

Table II.3.3. Comparison of Results from Evaluators A and B

Sample Data	Mean of results Didacs 1&2 Evaluator A			Mean of results Didacs 1&2 Evaluator B		
	Mean Value	σ 1)	n 2)	Mean Value	σ 1)	n 2)
Orange C141						
Energy Range 5.53 - 4.80 MeV normal evaluation	2.9867	0.0040	13	2.9870	0.0027	9
Blue D191						
Energy Range 5.53 - 4.80 MeV normal evaluation	1.6372	0.0032	3	1.6384	0.0023	13

1) Standard deviation of single measurement, based on the stated number of measurements

2) Number of measurements

In the anion exchange column separations used the behaviour of the trivalent actinides is chemically identical. Therefore the decontamination factors for ^{242}Cm and ^{244}Cm were used as a measure of the decontamination factor for ^{241}Am.

3.5 Results

Table II.3.4 Best Alpha-Activity Ratios and Accuracies from Harwell Characterization

Sample	Activity ratio	Accuracy [x] (%)	Number of measurements
B 89	1.4455	± 0.30	21
C 141	2.9866	± 0.30	22
D 191	1.6382	± 0.30	16

Data from A41 and A33 is not included as characterization data because the solution was found to be inhomogeneous.

3.6 Assessment of Uncertainties

By comparing the values for the ^{238}Pu/(^{239}Pu + ^{240}Pu) activity ratio in Table II.3.4. with the values listed in Tables II.3.2. and II.3.3. the following uncertainty estimates have been made.

(1)	Instrumental uncertainty	0.07 %
(2)	Evaluation method uncertainty	0.03 %
(3)	Evaluator uncertainty	0.01 %

Since the estimated uncertainties are small and the numbers of evaluations used to derive them are also small it should be stressed that too much significance should not be attached to these numbers, other than as an indication that large uncertainties were not introduced into the characterization procedures.

Other sources of systematic uncertainties are

(4) The uncertainty due to residual ^{241}Am contamination in the plutonium fraction at the time of final separation is estimated to be $< 0.02\%$ by analogy with the decontamination factor of 4×10^4 measured

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[x] See App. 2 for the statement of accuracy.

for ^{244}Cm. Determination of the ^{241}Am content of the purified plutonium solution by alpha and gamma measurements failed to give a significant result. In both cases a value of < 0.05 % was obtained.

(5) Uncertainty in the (^{239}Pu + ^{240}Pu) activity at Nov. 1, 1977 from ^{244}Cm decay ≈ 0.0006 %.

(6) Uncertainty in the ^{238}Pu activity at Nov. 1, 1977 from ^{242}Cm decay ≈ 0.008 %.

3.7 Conclusions

The procedures carried out in the characterization of samples B, C and D do not differ in any way from normal standard procedures practised in this laboratory, other than in the number of sources and measurements requested for each sample. It has always been recognised that the preparation of thin uniform sources, with care and attention to detail is crucial to the success of alpha spectrometry measurements. Thin uniform quantitative sources can easily be prepared using the TEG spreading technique.

The philosophy adopted at Harwell in alpha spectrometry measurements has always been that the correct approach is to prepare sources for analysis which are thin and uniform, so that analyser data processing facilities will give results sufficiently accurate for the majority of routine measurements, and the application of tailing corrections is seldom necessary. Bearing in mind the problems of self absorption, source non uniformity and variations between sources which are difficult to predict and quantify, the use of computer programmes to evaluate thick source spectra is difficult and time consuming and can be avoided by the preparation of thin sources using the simple well tried TEG spreading technique.

4. CHARACTERIZATION OF AS-76 SAMPLES BY MASS SPECTROMETRY AT NBS, WASHINGTON

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The isotopic compositions of four CBNM plutonium samples, Ae3112, Bd212, Ce3112 and De2121, were determined by thermal ionization mass spectrometry. The samples, received as a dry residue in glass vials containing 20-50 μg of plutonium, were dissolved in HNO_3 (1+2) and transferred to an anion exchange column. Americium and other impurities were eluted with HNO_3 (1+2) before removing the plutonium in a dilute nitric acid-hydrogen peroxide solution. After evaporation of the solution to dryness, the plutonium was further purified on a second anion exchange column using the same elution procedure. The solution was then evaporated to dryness and the residue dissolved in HNO_3 (1+19) to a concentration of approximately 25 μg of plutonium per ml of solution.

The mass spectrometric procedure is similar to the method described for uranium in NBS Special Publication 260-27 /6/. A triple-filament rhenium ribbon ion source with approximately 200 ng of plutonium per sample was utilized. The plutonium was placed on the filament in approximately 10 microliters of nitric acid solution and evaporated to dryness with a heat lamp and 1.0A electric current for 10 minutes. The electric current was then adjusted in the following manner and time sequence :

1. 1.5A for 5 minutes;
2. 1.8A for 5 minutes;
3. dull red heat for approximately 20 seconds.

An average plutonium ion current intensity of 5-7 x 10^{-12}A was obtained for the ratio measurement. The plutonium isotopic ratios were measured in the following symetrical pattern : $^{239}Pu/^{240}Pu$; $^{241}Pu/^{240}Pu$; $^{242}Pu/^{240}Pu$; $^{238}Pu/^{240}Pu$; $^{242}Pu/^{240}Pu$; $^{241}Pu/^{240}Pu$; and $^{239}Pu/^{240}Pu$. Each ratio set consisted of ten individual ratio determinations. All measurements were completed within 24 hours after the separation of americium by ion exchange chromatography.

All isotopic ratios were corrected (Table II.4.1) for the effects of isotopic fractionation by analyzing uranium SRM U500 and was found to be 0.125 percent per mass unit. The calibration is based upon the assumption that, exclusive of ionization efficiency, the evaporation and ionization process for uranium and plutonium are identical. Since plutonium was estimated to be a factor of 5 more efficiently ionized than uranium, the

Table II.4.1. Isotopic Ratios of AS-76 Samples on 1 Nov. 1977 (corrected for isotopic fractionation)

		Sample	^{238}Pu/^{240}Pu	^{239}Pu/^{240}Pu	^{241}Pu/^{240}Pu	^{242}Pu/^{240}Pu
Mean value	$\bar{y}$	B	0.03365	2.7759	0.31523	0.12165
Standard deviation of single ratio determination	S(y) (%)		0.3	0.04	0.04	0.1
Number of measurements (10 ratio determinations each)	n		3	3	3	3
Uncertainty(SD)*)	(%)		± 2.1	± 0.25	± 0.25	± 0.4
Accuracy (3σ)°)	(%)		± 1.2	± 0.15	± 0.15	± 0.25
	$\bar{y}$	C	0.06872	2.6449	0.31637	0.13028
	S(y) (%)		0.16	0.04	0.04	0.1
	n		3	3	3	3
Uncertainty(SD)*)	(%)		± 1.0	± 0.25	± 0.25	± 0.4
Accuracy (3σ)°)	(%)		± 0.6	± 0.15	± 0.15	± 0.25
	$\bar{y}$	D	0.03696	2.5929	0.32012	0.13635
	S(y) (%)		0.3	0.04	0.04	0.1
	n		3	3	3	3
Uncertainty(SD)*)	(%)		± 1.9	± 0.25	± 0.25	± 0.4
Accuracy (3σ)°)	(%)		± 1.1	± 0.15	± 0.15	± 0.25

*) The indicated uncertainty is for a Single Determination and for a 95 % confidence level. It is based upon a judgement of the error in determining the correction for isotopic fractionation using uranium.

°) Note from the coordinator : NBS and CBNM used the same standard reference materials for the determination of the correction for isotopic fractionation via measurements of the ^{239}Pu/^{240}Pu ratios. Accuracies to the mean values and for 99.7 % (3σ) confidence level have been calculated by the coordinator.
As explained in the CBNM paper Ch. II.5., the accuracies were obtained by multiplying the stated uncertainties with a factor 0.57.

uranium sample size was adjusted to 1 μg per sample filament to yield the same ion current intensity as 200 ng of plutonium per sample filament. The indicated uncertainty in Table II.4.1 is based upon the precision of the ratio measurement and upon a judgement of errors in the determination of the mass dependent correction for isotopic fractionation using uranium /6/.

All measurements were carried out during the period 25-28 Oct. 1977. The isotopic composition values reported in Table II.4.2 have been adjusted to a base date of 1 Nov. 1977 using a NBS determined ^{241}Pu half life of 14.36 ± 0.09 a.

Table II.4.2. Isotopic Composition of AS-76 Samples on 1 Nov. 1977

Sample	Atom %				
	^{238}Pu	^{239}Pu	^{240}Pu	^{241}Pu	^{242}Pu
B	0.792	65.373	23.550	7.420	2.865
C	1.652	63.579	24.038	7.599	3.132
D	0.904	63.459	24.473	7.827	3.337

5. CHARACTERIZATION OF AS-76 TEST SAMPLES BY MASS SPECTROMETRY AT CBNM, GEEL

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JRC-CBNM, Geel, Belgium

The plutonium isotopic compositions of the solutions Ae3113, Bd213/Be3111, Ce3113 and De2122 (Fig. I.4 to I.7) have been measured by thermal ionization mass spectrometry. The samples were purified on an anion exchange column to remove uranium, americium and fission products. Three successive purification procedures, as described in Ch. I.6., were carried out. The plutonium fraction collected from the column was evaporated to dryness and the residue dissolved in 1M HNO_3 to a concentration of approximately 1 mg Pu/ml.

The mass spectrometer used was a 12 inch 90 degrees analyser type, equipped with a triple filament rhenium ribbon ion source and Faraday cage collection. Approximately 2 μg of plutonium were used per source loading. The isotope ratios were measured on constant total ion currents (2-3 x 10^{-11}) and filament temperatures, and using standardized procedures for the sequence of measured ratios, filament heating patterns and duration of the measurement cycles. The $^{238}Pu/^{239}Pu$ ratio was carefully monitored after each of the three purification runs for trend and reproducibility as these are highly sensitive indicators for contributions from isobaric ions, for instance uranium. Also the absence of mass 235 ions - indicative for uranium - was systematically checked. At least six ratio determinations were obtained per filament loading.

The measured ratios have been corrected for isotopic fractionation using a calibration factor R_{ref}/R_{obs} obtained from a number of measurements of the $^{239}Pu/^{240}Pu$ ratio in the NBS reference materials SRM 946, 947 and 948. The corrected atom ratio R_C is obtained from the measured ratio R_M and the correction factor for isotopic fractionation R_{ref}/R_{obs} according to $R_C = R_M \cdot R_{ref}/R_{obs}$. A calibration chart, covering the period 1977-1978 during which the AS-76 measurements were carried out, is shown in Fig. II.5.1. Statistical parameters derived from that distribution are given in Table II.5.1. The atom ratios have further been corrected for the decay of ^{238}Pu and ^{241}Pu to the reference date of 1 Nov. 1977.

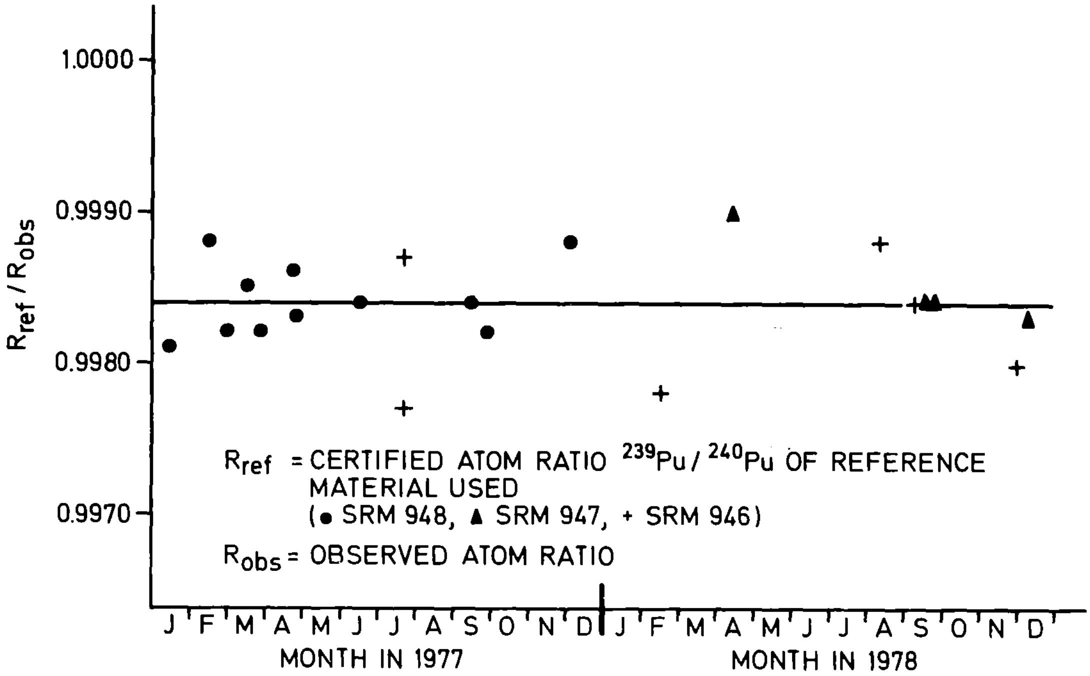

Fig. II.5.1 Calibration chart for $^{239}Pu/^{240}Pu$ measurements over the period 1977 and 1978 using different NBS RM's.

Table II.5.1. Random Uncertainty of the Correction Factor for Isotopic Fractionation. (See also Fig. II.5.1).

Mean value	$S(y)$ (%) 1)	$S(\bar{y})$ (%) 2)	$t_{(3\sigma,21)}\ S(\bar{y})$ (%) 3)
0.9984	0.03	0.007	± 0.024

1) Sample estimate of the standard deviation for a single determination (from the distribution of Fig. II.5.1).

2) Sample estimate of the standard error of the mean (from n = 21 determinations).

3) Random uncertainty for the mean at the 3σ confidence level. It is obtained from the value in the previous column 2) as ± $t.S(\bar{y})$, applying a Student's t-value of 3.4.

Table II.5.2. Accuracy of the Atom Ratio ^{239}Pu/^{240}Pu of NBS Standard Reference Materials used for Calibration.

NBS Standard Reference Material	Atom Ratio ^{239}Pu/^{240}Pu		
	Value on 1 Nov. 1977 1)	Overall uncertainty SD (95 %) (%) 2)	Accuracy (%) 3)
SRM 946	6.8909	± 0.14	± 0.08
947	4.1410	± 0.15	± 0.09
948	11.5730	± 0.14	± 0.08

1) Certificate value corrected for the decay of ^{240}Pu and ^{239}Pu. In Fig. II.5.1 this correction is done to the date of measurement of each individual point.

2) Overall uncertainty for a Single Determination and for a 95 % confidence level. This value is calculated as the linear sum of the relative uncertainties (SD 95 %) on the ^{239}Pu and ^{240}Pu isotope abundances stated in the NBS certificates. (Since the uncertainties on the ^{239}Pu and ^{240}Pu abundances are always obtained from the uncertainty on the measured ratio of ^{239}Pu/^{240}Pu it would be preferable to state also the latter uncertainty on the certificates).

3) This accuracy is in accordance with App. 2. It is obtained from the value in the previous column 2) and based on an arbitrary number of determinations n = 10 and Student's t-values at 95 % and 99.7 % confidence levels of 2.23 and 4.0, respectively; hence,

$$3) \approx \frac{2)}{\sqrt{10}} \; \frac{t(99.7\ \%)}{t(95\ \%)} = 2) \times 0.57$$

The accuracy on the ^{239}Pu/^{240}Pu ratio of the reference materials is given in Table II.5.2. The accuracy of the correction factor for isotopic fractionation is then obtained from the data in the two Tables as 0.024 + 0.08 ≈ 0.10 (%). The ^{239}Pu/^{240}Pu ratio in the assayed sample is determined by carrying out three runs (filament loadings) with six scans each (ratio determinations). Since the reference materials and assayed samples are purified and measured under identical conditions, one can postulate that the $^{239}Pu/^{240}Pu$ ratios measured in the assayed samples will basically follow the same statistical distribution as in Fig. II.5.1. In case of a normal distribution with known standard deviation σ = 0.03 %, the random uncertainty for the mean $^{239}Pu/^{240}Pu$ atom ratio in the assayed sample and for a 3σ confidence level (z = 3) is obtained from $z\,\sigma/\sqrt{n}$. For n = 3 this becomes 0.05 (%). If one considers a typical sample estimate for the standard deviation of S(y) = 0.04 % (Table II.5.3), the random uncertainty for the mean of three runs and for a 3σ confidence level (t = 9.2) would be $t\cdot S(y)/\sqrt{n}$ = 0.2 %. Adopting a value of 0.15 % for the 3σ random uncertainty and with an accuracy of 0.1 % for the correction factor for isotopic fractionation, the accuracy for the mean $^{239}Pu/^{240}Pu$ ratio in the assayed sample becomes 0.15 + 0.1 = 0.25 % (Table II.5.3). An additional uncertainty of 0.5 % is considered in estimating the accuracy of the measured atom ratios $^{238}Pu/^{239}Pu$. This is based on a judgement of:

- a possible interference from ^{238}U with the signal at mass 238, and

- an overall uncertainty from the application of the same correction factor for isotopic fractionation to atom ratios considerably smaller than those of the RM's used in the calibration chart of Fig. II.5.1. We have verified on uranium that this correction factor is constant for atom ratios $^{235}U/^{238}U$ ranging from 10^{-2} to 25, provided the thermal ionization parameters are carefully controlled /7/.

Table II.5.3 shows the results and accuracies of the measured atom ratios for the samples B, C and D. All results were corrected to the reference date of 1 Nov. 1977. Table II.5.4 shows the isotopic composition of the samples B, C and D at the same reference date. Since the sample A was found to be inhomogeneous, no results are given for that sample.

Table II.5.3. Atom Ratios in AS-76 Samples on 1 Nov. 1977

		Sample	^{238}Pu/^{239}Pu	^{239}Pu/^{240}Pu	^{241}Pu/^{240}Pu	^{242}Pu/^{240}Pu
Mean value	$\bar{y}$	B	0.012207	2.7762	0.31517	0.12155
Standard deviation of single ratio determination (run)	S(y) (%)		0.1	0.04	0.04	0.1
Number of runs (6 ratio determinations each)	n		3	3	3	3
Accuracy *)			± 0.8	± 0.25	± 0.25	± 0.3
	$\bar{y}$	C	0.025958	2.6458	0.31588	0.12982
	S(y)(%)		0.1	0.04	0.04	0.1
	n		3	3	3	3
Accuracy	(%)		± 0.7	± 0.25	± 0.25	± 0.3
	$\bar{y}$	D	0.014362	2.5933	0.31966	0.13615
	S(y)(%)		0.1	0.04	0.04	0.1
	n		3	3	3	3
Accuracy	(%)		± 0.8	± 0.25	± 0.25	± 0.3

*) See text.

Table II.5.4. Isotopic Composition of AS-76 Samples on 1 Nov. 1977

Sample	Atom %				
	^{238}Pu	^{239}Pu	^{240}Pu	^{241}Pu	^{242}Pu
B	0.798	65.372	23.547	7.421	2.862
C	1.651	63.598	24.037	7.593	3.121
D	0.911	63.462	24.472	7.823	3.332

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Appendix 1.

Data of interest for the preparation and measurement of AS-76 α-spectrometric sources

	Specific α-activity Bq/μg [x)]
^{238}Pu	$6.33\ 10^5$
^{239}Pu	$2.29\ 10^3$
^{240}Pu	$8.40\ 10^3$
^{241}Pu	$9.14\ 10^1$ (specific β activity is $3.73\ 10^6$ Bq/μg)
^{242}Pu	$1.45\ 10^2$
^{241}Am	$1.27\ 10^5$

Approximate values			
Sample	α Activity (Bq/μg Pu)	$(^{241}\mathrm{Am}/^{238}\mathrm{Pu})_\alpha$ (per day after separation)+)	α-Activity Ratio $^{238}\mathrm{Pu}/(^{239}\mathrm{Pu}+^{240}\mathrm{Pu})$
A	4450	$2.5\ 10^{-4}$	0.4
B	8500	$2.4\ 10^{-4}$	1.4
C	13900	$1.2\ 10^{-4}$	3.0
D	9200	$1.9\ 10^{-4}$	1.6

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x) The Becquerel (Bq) is the unit of activity; 1 Bq = s^{-1} /1/.

+) ^{241}Am from the decay of ^{241}Pu grows into a freshly separated plutonium fraction at a rate of

$$\left(\frac{^{241}\mathrm{Am}}{^{238}\mathrm{Pu}}\right)_\alpha = 2.6 \cdot 10^{-5} \left(\frac{^{241}\mathrm{Pu}}{^{238}\mathrm{Pu}}\right)_{\mathrm{At}} \quad \text{per day.}$$

The indices α and At indicate the α-activity ratio and atom ratio, respectively. The linear relationship is acceptable for a time period of some 20 days.

Appendix 2

The Statement of Accuracy

Results which claim reliability must be stated as a value (which is usually a mean value) with a well defined uncertainty. The principle of an uncertainty being composed of random components and of systematic components is generally accepted but different philosophies exist about how to calculate and how to present it.

For the purpose of the AS-76 characterization results, uncertainties are expressed as "accuracies". According to the ICRU Report 12, Sept. 15, 1968, "accuracy" (or "overall uncertainty") means an estimate of the possible divergence of the quoted result from the true value. The accuracy is arbitrarily calculated as the sum of a random component for a 99.7 % (3σ) confidence level (assuming a normal distribution for the results) and a systematic component according to

$$\pm \left(t \frac{S(y)}{\sqrt{n}} + \Sigma e\right)$$

where: t is Student's t value for a 99.7 % (3σ) confidence level. t-Values for different confidence levels and sample sizes can be found e.g. in the NPL publication /4/.

$S(y)$ is the sample estimate of the standard deviation for a single determination, hence for unweighted observations

$$S(y) = \sqrt{\frac{\sum_{i=1}^{n} (y_i - \bar{y})^2}{n-1}}$$

where $\bar{y}$ is the average from n determinations y_i, $i=1,n$.

Σe is the estimated bound to systematic uncertainties.

Appendix 3

Half-lives, Alpha-Particle Energies and Relative Intensities

^{238}Pu	(87.74±0.09)a	/8/
I_α (%)	E_α (keV)	/9/,/10/
71.6	5499.21	
28.3	5456.5	
0.10	5357.7	
0.003	5205.6	

^{239}Pu	(24110.±30)a	/8/
I_α (%)	E_α (keV)	/9/,/11/
73.3	5155.4	*)
15.1	5142.9	
<0.03	5112.	
11.5	5104.6	
0.036	5076.	
0.025	5054.	

^{240}Pu	(6553±8)a	/8/
I_α (%)	E_α (keV)	/9/,/12/
73.4	5168.3	
26.5	5123.8	
0.091	5014.	
0.002	4851.	

^{241}Pu	$(6.0\pm.1)10^5$a (α)	/8/
I_α (%)	E_α (keV)	/9/,/13/
0.35	5054.	
1.02	5042.	
0.41	4998.	
1.3	4972.	
83.2	4896.5	
12.1	4853.5	
1.2	4799.	
0.2	4784.	

^{242}Pu	$(3.76+0.02)10^5$a	/8/
I_α (%)	E_α (keV)	/9/,/14/
77	4900.9	
23	4856.6	

^{241}Am	(432.6±0.6)a	/8/
I_α (%)	E_α (keV)	/9/,/13/
0.34	5544.3	
0.20	5512.	
85.2	5485.74	
<0.04	5469.	
12.8	5442.98	
0.01	5417.	
1.4	5388.	

The stated uncertainty to the half-life values is about 1/3th the accuracy in the sense of App. 2.

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*) Recent measurements at BIPM indicate a higher value: A. Rytz, Bureau International des Poids et Mesures, Sèvres, France, private communication (1979).

Appendix 4.

Preparation of Drop Deposition Sources with TEG added as a Spreading Agent

In the analytical control of chemical separations of actinide elements, where accurate qualitative and quantitative measurements of absolute disintegration rates of the individual constituents of an alpha source containing several nuclides is required, a thin source is essential. The most suitable method for preparing accurate quantitative sources which are sufficiently thin for alpha spectrometry measurements is by using Tetra Ethylene Glycol (TEG) as a spreading agent.

The procedure is as follows :

1. A previously cleaned polished stainless steel disc (tantalum for HCl and HF solutions) is mounted on to a sindanyo square by painting a rim of zapon round the source tray. This serves to attach it to the sindanyo when dry and also serves to define the source area on the stainless steel.
2. An accurate aliquot of the solution to be assayed is weighed or pipetted on to the stainless steel disc and a drop of TEG is added, or alternatively a 10 % solution of TEG in water may be used.
3. The source is warmed under an infra red lamp and the TEG polymerises. Provided that the tray is rotated continually during the drying off period, a thin deposit is obtained.
4. When polymerisation is complete the disc is ignited, leaving an adherent oxide deposit, which would normally be indicated by a slight stain on the disc.

Using this technique, sources prepared from chemically clean solutions can give resolutions of $<$ 20 KeV FWHM.

Appendix 5.

Preparation of Vacuum Evaporated Sources

The vacuum evaporated sources for AS-76 were prepared as follows : 5µl of the plutonium solution was deposited in a dimple located in the centre of a 0.002" tungsten filament, the ammonium salts were sublimed off at atmospheric pressure at a low temperature (≈ 200°C). Volatile impurities were then pre-fired off the filament onto a dummy backing disc under reduced pressure at approximately 500°C. Finally the plutonium was evaporated off on to a polished stainless steel backing disc at approximately 2500°C. It is necessary to maintain the vacuum at a pressure of at least 10^{-3} Pa during evaporation to prepare high quality sources.

Appendix 6

Inhomogeneity in Sample A and local Differences in the Plutonium Isotopic Concentration.

We consider the situation of the solution Ab3 (Fig. I.4.) which contains about $6.9 \cdot 10^{-3}$ mg ^{238}Pu and calculate the amount of ^{239}Pu and ^{240}Pu which would explain the difference between the results for A22 and Ac33 in Fig. II.1.2.

The following notations are used:

G_i	amount of plutonium isotope i (mg)
T_i	half-life value of plutonium isotope i
Δ_i	change of the amount of material of isotope i (mg)
R_α	α-activity ratio ^{238}Pu/(^{239}Pu + ^{240}Pu)
R_{MS}	atom ratio ^{239}Pu/^{240}Pu

For the material in vial A22 one may write

$$R_{MS1} = \frac{G_{239}}{G_{240}} = 5.127 \qquad (1)$$

$$R_{\alpha 1} = \frac{G_{238}/T_{238}}{\dfrac{G_{239}}{T_{239}} + \dfrac{G_{240}}{T_{240}}} = 0.3915 \qquad (2)$$

Replacing G_{239} by $G_{239} + \Delta_{239}$ and similarly for G_{240} one obtains two further similar expressions for the material in vial Ac33

$$R_{MS2} = 5.085 \qquad (3)$$

$$R_{\alpha 2} = 0.404 \qquad (4)$$

Solving these equations in the unknowns one obtains

$G_{239} = 2.82$ mg
$G_{240} = 0.55$ mg
$\Delta_{239} = -0.097$ mg
$\Delta_{240} = -0.015$ mg

Expressing the amounts Δ_i relative to the amounts of spike added one obtains

$$\frac{\Delta_{239}}{2.32} = 4.1 \cdot 10^{-2} \quad \text{and} \quad \frac{\Delta_{240}}{0.30} = 4.8 \cdot 10^{-2}$$

This means that the difference between the results of A22 and Ac33 can be understood as a virtual loss of approximately equal fractions of the ^{239}Pu and ^{240}Pu spike materials. It can easily be shown that "losses" of equal fractions of the ^{239}Pu and ^{240}Pu spike materials do result into a linear relationship as represented in Fig. II.1.2.

Appendix 7

Packaging of Samples and Shipment Requirements.

The samples A, B, C, D and E were shipped as dry residues in glass vials with plastic cap. Each vial has been packed in a double plastic bag. All five samples were put in one steel container which was put in a second steel container (Fig. A.1.), the interspace being filled with vermiculite. The second steel container is an integral part of the Type B (U) container into which it is placed. The interspace is filled with discs of "Thermax S" (on the basis of vermiculite) or with asbestos cement. The Type B (U) container (Fig. A.2.) is approved by the Belgian "Ministerie van Volksgezondheid en van het Gezin".
The container has the identification mark

EURATOM
B/7601/B (U).

The Belgian Authoritie's approval B/7601/B (U) of this container was sufficient for shipping samples to a number of countries, however some other countries had special requirements.

U.S.A. Import of radioactive material to, or export from the USA in type B container is subject to a certificate revalidated by the Department of Transportation, Washington D.C. The samples have been shipped by air freight, in accordance with the IATA Restricted Articles Regulations, 20th edition.

Japan Present Japanese regulations required a certificate of the Type B (U) container approved by the government of Japan for the import of plutonium into, and export from Japan. The Belgian certificate B/7601/B (U) was mailed to the participating laboratory which returned the governmental approval to CBNM by cable.

Federal Republic of Germany The Plutonium samples were sent by road transport. The samples for Berlin were shipped by air. In both cases the following documents were needed:

i) transport authorization from the "Physikalisch-Technische Bundesanstalt" (PTB), Braunschweig
ii) a contract of liability insurance with the "Deutsche Kernreaktor Versicherungsgemeinschaft", Köln.

Shipment to Berlin required in addition a transport authorization from the "Senator für Berlin" in Berlin.

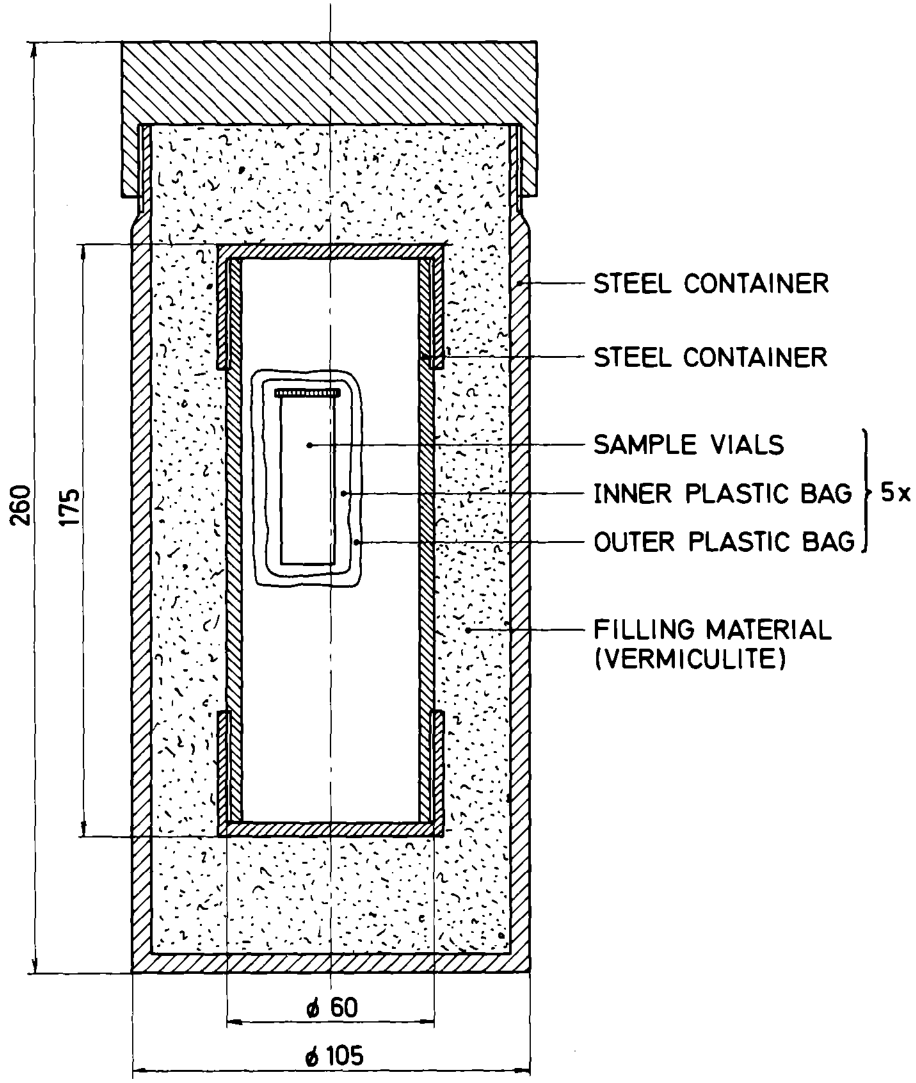

Figure A1 Packaging of the AS- 76 samples.
This assembly is packed in a B(U) container.

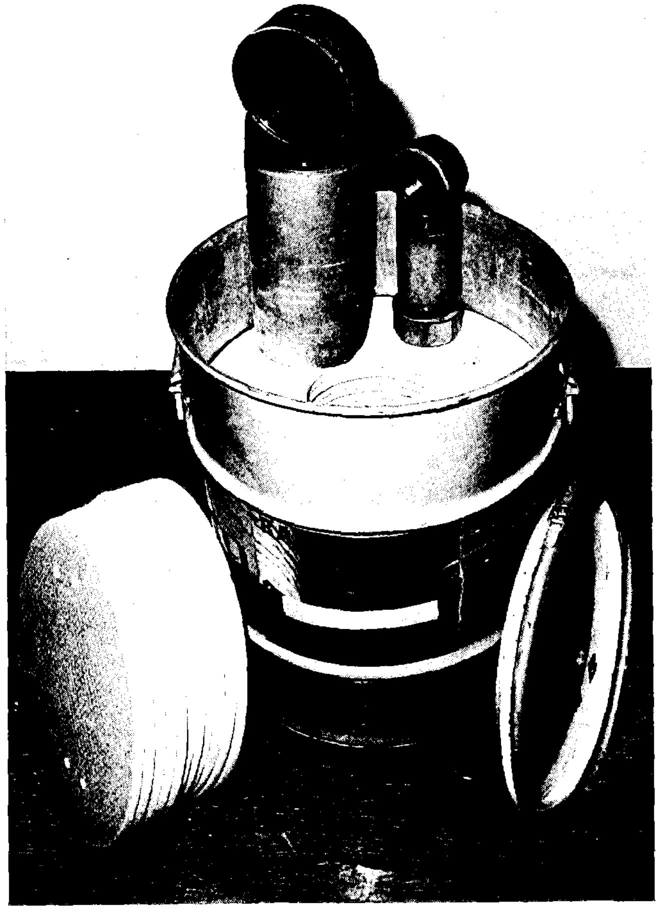

Figure A2 Inner steel containers and type B (U) container used for shipment of AS - 76 samples. (hight 425 mm, diam. 322 mm, total weight ≈ 35 kg).