Results from the ^{237}Np exercise

EUROMET action 416

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(based on contributions from the participants to Euromet action 416)

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ABSTRACT

This report is based on contributions from the many participants to the Euromet project, "action 416", which was entitled "^{237}Np research into problems relating to purification, characterisation and standardization". Primary standardizations were made by the defined solid angle method, coincidence methods, $4\pi\alpha$ counting, $2\pi\alpha$ counting, and by liquid scintillation. Absolute X-ray, gamma-ray and alpha-particle emission probabilities were also determined. Secondary standardizations were made with calibrated gamma-ray spectrometers.

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1. INTRODUCTION

A proposal to establish a collaborative project to study the actinide ^{237}Np was agreed in May 1997, involving initially eight partner institutions, with M J Woods (NPL) acting as the coordinator. The project, EUROMET action n^{o} 416, was entitled "^{237}Np research into problems relating to purification, characterisation and standardization".

Because of its long half-life of $2.14*10^{6}$ years, ^{237}Np will exhibit an increasingly important profile in the inventory of radioactive materials in the environment, resulting from its production and subsequent release from the nuclear power cycle.

The ^{237}Np is produced as a long lived waste product in nuclear reactors via either the action of thermal neutrons on ^{235}U,

$$^{235}\mathrm{U}(\mathrm{n},\gamma)^{236}\mathrm{U}(\mathrm{n},\gamma)^{237}\mathrm{U}\xrightarrow{\beta-}{}^{237}\mathrm{Np},$$

or the action of fast neutrons on ^{238}U,

$$^{238}\mathrm{U}(\mathrm{n},2\mathrm{n})^{237}\mathrm{U}\xrightarrow{\beta-}{}^{237}\mathrm{Np}.$$

It is thus of great importance for both long term storage considerations and environmental monitoring of effluent streams. Surprisingly, no absolute standardizations of this radionuclide have been reported. In addition, previous studies of the decay data of ^{237}Np have failed to produce a reliable and consistent decay scheme (e.g. *Woods et al,1988 ; Lowles et al, 1990*). The main problem is in balancing the level scheme and in determining the emission probabilities associated with the very low energy gamma transitions (5.2, 8.0 and 9.8 keV).

It is important that the characteristics of this radionuclide are well defined and that agreement on primary standards of ^{237}Np is established internationally. Primary standards may be established using the 'conventional' techniques but their subsequent dissemination to the user community and the ability of that community to use secondary standards and analytical techniques relies on a sufficiently accurate set of decay scheme data, particularly, alpha and gamma emission probabilities and the half-life value.

The ability to determine such data and standards also requires a high level of radioactive purity. This EUROMET project was designed to provide that data and to demonstrate "equivalence" between national standards.

The initial plans included the following items.

a) Preparation of a suitable ^{237}Np solution

b) Confirmation of the ^{237}Np/^{233}Pa equilibrium state by ionization chamber and γ-spectrometry.

c) Standardization of the ^{237}Np solution. The techniques used for standardization were to be the prerogative of the participating laboratory but it was hoped that primary standardization would be included, where possible. This will be necessary if the measurement is to be included in the equivalence reference value.

d) Determination of contaminant levels

e) Determination of gamma emission probabilities. The principal user bases for standards of ^{237}Np are those involved in environmental monitoring and nuclear waste. The gamma lines of most interest to them will be those which are most abundant, particularly the 86, 312 and 340 keV lines, although for nuclear structure studies, all lines are important. Present uncertainties of gamma emission probabilities of the significant lines range from about 1% (312 keV) to 6% (86.6 keV) The general consensus is that an accuracy of at least $\pm$ 1% is required.

f) Determination of alpha emission probabilities.

High accuracy relative alpha-particle emission probabilities were determined at IRMM in 1990 (Bortels 1990). However, these were not derived by comparing individual alpha-particle peaks with the activity of the ^{237}Np source, but by assuming a 100% alpha-decay. A new determination using a standardised source should result in absolute values. This Euromet project should also lead to a better balanced decay scheme.

g) Determination of mass concentration of Np (g/g). By linking this to the

equivalence reference activity value, a new value for the half-life could be determined.

2. ^{237}Np MAIN CHARACTERISTICS

The actinide ^{237}Np can be considered as the first member of a long disintegration chain, leading eventually to the stable isotope ^{209}Bi. The ^{237}Np itself has a long half-life (2.14 ± 0.01)*10^6 years and undergoes 100% alpha decay to ^{233}Pa, which has a short half-life (27.0 ± 0.1) days and undergoes 100% beta decay to another long lived nuclide ^{233}U.

Due to the relative half-lives involved, only the two leading members of the chain, ^{237}Np and ^{233}Pa, contribute significantly to the measurements in this project. Both of these nuclides produce gamma rays and conversion events. After several ^{233}Pa half-lives, the ^{237}Np and ^{233}Pa will reach secular equilibrium, with essentially equal activity of these two nuclides.

Figures 1 & 2, illustrate the decay schemes of ^{237}Np and ^{233}Pa respectively. Figure 3 shows a typical gamma-ray spectrum.

3. SOURCE MATERIAL

An early barrier to progress had been the lack of sufficiently pure material but in 1997 suitable material was identified at the Institute for Reference Materials and Measurements, the EC Joint Research Centre at Geel in Belgium. Purification and preparation of this material was undertaken at IRMM from 1997-08-19 to 1997-08-22 by S M Jerome (NPL) with the help of IRMM staff (M Bickel, C Hill, W Leidert, R Pilvio, D Reher and G Sibbens).

The starting material was a solution of ~2.5g NpO_2 in ~36g of 7M HNO_3, equivalent to an activity concentration of ~1.6 MBq/g. Since the ^{237}Np used had been produced as a by-product of nuclear fuel reprocessing, there was the possibility that the material was contaminated with small amounts of plutonium isotopes, mainly ^{238}Pu *(Sutton, 1995).* It was therefore necessary to reduce the plutonium concentration to levels where the standardization of the ^{237}Np was not affected : in practice, this requires a level of <0.1% in activity terms.

The most straightforward way of doing this is by anion exchange chromatography and this affords a simple and very specific way of resolving a mixed solution of thorium, protoactinium, uranium, neptunium, plutonium and the trivalent actinides (actinium and the elements beyond and including americium in the periodic table). The resin used was Bio-Rad AGI-X8 (200-400 mesh), which was made up into a resin bed of 10mm diameter and 250mm length.

Under the conditions existing in the ^{237}Np solution, the thorium, protoactinium, uranium, neptunium and plutonium are preferentially adsorbed onto the column *(Faris and Buchanan, 1964; Korkisch 1989)*. The column was washed with ~100 cm^3 8M HNO_3 to remove any residual trivalent actinides: under these conditions any uranium present is mostly removed from the resin. The column was then washed with ~100 cm^3 12M HCl: thorium does not form an anion complex with the chloride ion and is therefore washed from the column. To resolve the neptunium and plutonium, the column was then washed with ~100 cm^3 12M HCl that was 0.1M with respect to NH_4I. This reagent is a mild reductant that reduces $Pu^{>3+}$ to Pu^{3+}; plutonium in this oxidation state behaves as the other trivalent actinides and is washed from the column, since it does not form an anionic complex with the chloride ion.

Finally, neptunium was washed from the column with 1M HCl and collected. This solution was adjusted to ~5M with respect to HCl, and oxalic acid was also added, to a concentration level of ~33 μg/g of solution, to act as a complexant for the ^{233}Pa daughter in order to keep it in solution. This solution was found to contain <0.12% of plutonium, by activity (see below).

The solution was quantitatively dispensed to 64 BIPM standard 5ml ampoules at IRMM at the end of 1997. Before dispensing the active solution all ampoules were cleaned and rinsed with the carrier solution of 6M HCI + 33ug/g oxalic acid (see Table 3). All ampoules were measured in the secondary standard ionization chamber of IRMM to verify correct filling, homogeneity and secular equilibrium between ^{237}Np and ^{237}Pa. In February 1998, 42 ampoules were shipped to NPL who performed similar measurements. The remaining 22 ampoules were measured again during March and April 1998 at IRMM resulting in a spread of 0.08% of the ionization chamber response per unit mass. The results of the first 5 ampoules remaining at IRMM were significantly lower than the rest of the batch which might be

allocated to an initial adsorption effect of the dispensing equipment. Ampoules were subsequently distributed to the participants. Table 1 records the ampoule identifiers, masses and destinations.

Table 1: Ampoule identifiers with mass of neptunium solution and destination.
Each ampoule is identified by IRMM codes 9706 to 9769 and also by NPL codes A86/98 - A127/98.
Ampoules with no destination specified remain in storage at NPL.
The standard uncertainty of each ampoule mass is 0.001% or 0.00004g.

identifier		mass g	destination		identifier		mass g	destination
9706	A86/98	4.05666			9739	A107/98	4.05943	CIEMAT
9707	A87/98	4.02574			9740	A108/98	4.06793	
9709	A88/98	4.07684			9742	A109/98	4.06321	
9710	A89/98	4.05817			9743	A110/98	4.05201	BIPM
9711	A90/98	4.04826			9745	A111/98	4.07071	
9714	A91/98	4.07198			9746	A112/98	4.04762	
9715	A92/98	4.07058	NIST		9749	A113/98	4.06996	NIST
9717	A93/98	4.07126			9750	A114/98	4.06023	NPL
9718	A94/98	4.07027	BNM-LNHB		9752	A115/98	4.06654	
9720	A95/98	4.07015			9753	A116/98	4.06002	
9721	A96/98	4.04708	IRMM		9755	A117/98	4.06967	
9723	A97/98	4.07274	CIEMAT		9756	A118/98	4.06832	NRCC
9724	A98/98	4.07293			9758	A119/98	4.06512	IRMM
9726	A99/98	4.04815	NRCC		9759	A120/98	4.06594	
9727	A100/99	4.16494	BIPM		9761	A121/98	4.06687	
9729	A101/98	4.05279	BIPM		9762	A122/98	4.06162	BNM-LNHB
9730	A102/98	4.04264			9764	A123/98	4.05095	PTB
9732	A103/98	4.05609	PTB		9765	A124/98	4.05059	
9733	A104/98	4.07163			9767	A125/98	4.06741	BIPM
9736	A105/98	4.06430	BNM-LNHB		9768	A126/98	4.06498	

9737	A106/98	4.06959			9769	A127/98	4.06528	

4. PURITY AND NOMINAL ACTIVITY

Preliminary IRMM measurements indicated a nominal ^{237}Np activity of 139 ± 24 kBg/g and the presence of ^{238}Pu and ^{239}Pu impurities. These results, along with details of impurity measurements made by CIEMAT and PTB, were as follows:

The mass ratio (%g/g) in Table 2 is determined by alpha-particle spectrometry.

Table 2: Impurity measurements

	mass ratio (% g/g)	activity ratio (% Bq/Bq)			
participant	IRMM	IRMM		CIEMAT	PTB
method	alpha spectrometry	alpha spectrometry prelim	final	alpha spectrometry	alpha spectrometry
^{238}Pu/^{237}Np	0.0000019	0.047	0.051(7)	0.059	
^{239}Pu/^{237}Np	0.00074	0.066			
(^{238}Pu+^{239}Pu) /^{237}Np					0.103(4)
(^{239}Pu+^{240}Pu) /^{237}Np			0.067(9)	0.073	
^{243}Am/^{237}Np				0.018	
unknown/^{237}Np (possibly ^{244}Cm)				0.041	

The values in the table include an uncertainty (in brackets) if given by the laboratory.

Figure 4 shows the spectrum of a neptunium source in the PTB alpha spectrometer. The impurity activity ratios were determined from the ratios of counts in the respective regions of interest in the source spectra.

No gamma-emitting contaminants were detected by PTB using a Ge spectrometer in the region 10 keV to 2.7 MeV.

5. THE EQUILIBRIUM STATE OF ^{237}Np WITH ITS DAUGHTER ^{233}Pa.

A significant problem with any measurements of ^{237}Np is the state of equilibrium between the ^{237}Np and its daughter ^{233}Pa. Any disturbance of the equilibrium state requires a lengthy period (i.e. several multiples of the ^{233}Pa half-life) to elapse before restoration of equilibrium can be guaranteed. Earlier work at NPL showed that the mere act of transferring a solution from one ampoule to another sometimes significantly disturbed that equilibrium. Subsequent investigations suggested that this effect could be minimised, and possibly even eliminated, if the appropriate chemistry is used. To that end, the chemistry of the solution is as given in Table 3 and the density of the solution, based on that chemistry, is 1.11 g/cm^3.

Table 3: Chemistry of the solution

hydrochloric acid	5.8 mol/dm^3
oxalic acid	33 μg/g
total solids($NpCl_4$ + $(COOH)_2$)	8.6 mg/g (theoretical max 14.9 mg/g)

To check the equilibrium state, each ampoule prepared was assayed at NPL both in a high pressure ionization chamber and by Ge gamma spectrometry. For the ionization chamber, all ampoules were measured at the beginning and again at the end of March 1998. Since the majority of the response arises from the ^{233}Pa, any dis-equilibrium would be noticed relatively easily and seen as an increase in response with time. No such increase was found. For the gamma spectrometry, all ampoules were assayed at the beginning of March and a few again at the end of March 1998. The principal determinant was the ratio of peak areas from the 312 keV and 86 keV peaks, and no changes in these ratios were observable. On the basis of these results, it was concluded that the ampoules were homogeneous and that the solutions were in equilibrium.

Additional measurements of the equilibrium state were made by participating laboratories as follows:

a) NPL made stability checks by ionization chamber with solutions prepared by diluting the original solution with 6M HCl alone, and ampoules containing such solutions were found to be in equilibrium.

b) NRCC made ionization chamber measurements on ampoule A118/98 in June and

again in September 1998, and no change in activity was found, indicating that the ^{237}Np and ^{233}Pa were in equilibrium.

c) BNM-LNHB/IFIN-HH made gamma spectrometry measurements on solid sources prepared by weighing drops of the original solution onto Mylar foils (6μm thickness), which, after drying, were sealed with a further Mylar layer (as also used for photon-emission probability measurements). Over a period of 14 weeks, no significant change in the ratio of the 143 keV ^{237}Np γ-ray to various ^{233}Pa γ-rays was observed, within the estimated uncertainty of 0.4%.

6. DESPATCH OF AMPOULES TO PARTICIPANTS AND REFERENCE TIME

Given the problems with potential dis-equilibrium, it was decided to despatch ampoules to participants during May 1998, well in advance of the agreed reference time of 12 h UT 1 September 1998. This gave participants the option to prepare sources early, which would allow time for such sources to recover their equilibrium state, if it were disturbed during their source preparation.

NPL dispatched at least two BIPM ampoules, each containing approximately 4g of solution, to every participant, as noted in Table 2. Two of the ampoules sent to the BIPM were for measurement in the SIR system.

7. REPORTING FORMS

A reporting form, based on the BIPM type of form used for intercomparisons, was distributed to participants, who were encouraged to use the form or a variation based upon it. This was to enable as much relevant information as possible to be supplied in a consistent manner, although participants were at liberty to supply additional information.

For the standardization measurements, if satisfactory agreement is reached, it is hoped that the results can be used to demonstrate Equivalence (as understood by BIPM) between the participants. In order to be accepted as such, one of the criteria is that the comparison should be conducted in a “BIPM fashion”, which includes using the standard type of BIPM reporting forms.

8. PARTICIPATION

Because in most instances, the participants used very different techniques, and because some participants supplied minimal details whereas others gave quite extensive information, it is not easy to carry out a rigorous evaluation of the data and an analytical intercomparison of the various methods. Nevertheless, this report assembles the information, and attempts to compare and to analyse the results.

Eight laboratories have participated and contributed results to this EUROMET project no.416, as listed in Table 4.

Table 4: Participating laboratories and the staff responsible for the measurements

Laboratory	Address	Person(s) responsible for the measurements(s)
BIPM	Bureau International des Poids et Mesures SEVRES, France	C Michotte, C Colas
CIEMAT	Metroligía de Radiaciones Ionizantes Madrid, Spain	E García-Toraño, M T Crespo, L Rodriguez
IFIN-HH	National Institute of R&D in Physics and Engineering "Horia Hulubei". Bucharest-Magurele, Romania	A Luca
IRMM	Institute for Reference Materials and Measurements Geel, Belgium	B Denecke, G Sibbens
BNM-LNHB	Laboratoire National de Henri Becquerel Gif-sur-Yvette, France	J Bouchard, F Dayras, M Etcheverry, J Morel
NPL	National Physical Laboratory Teddington, UK.	P DeLavison, L Husband, D H Woods, S A Woods
NRCC	National Research Council Ottawa, Canada	D Santry, W Zhang
PTB	Physikalisch Technische Bundesanstalt Braunschweig, Germany	E Schönfeld, R Klein, H Janssen, E Günther, U Schötzig, H Schrader

Twelve activity measurements are reported, using 7 different methods. Six of the methods can be regarded as 'primary' measurements, although some of these may be considered as more 'absolute' than others, dependent on the various assumptions adopted or the extent or significance of the nuclear data that was assumed. Three laboratories performed secondary or relative activity determinations using gamma spectrometers calibrated with a range of other radionuclides.

Three laboratories measured absolute photon emission probabilities values and one participant reported absolute alpha emission probabilities.

Three laboratories determined the radioactive impurities present in the neptunium material.
Six laboratories made preliminary measurements using calibrated ionization chambers or spectrometers to estimate the activity. Six laboratories carried out adsorption measurements on the ampoules in which the solution was supplied.

9. PRELIMINARY MEASUREMENTS OF ACTIVITY

Laboratories were asked to make preliminary measurements of activity based on calibrated devices such as ionization chambers, well crystals or gamma spectrometers. This initial measurement is made on the original ampoule, and if possible, a second measurement is made after transfer of the solution to a new ampoule.

The total mass of solution found in the original ampoule was determined by some laboratories, enabling a comparison to be made with the dispensed weight as determined by IRMM according to the distributing laboratory (NPL).

Results at a reference time of 12h UT, 01.07.1998 are given in Table 5.

10. ADSORPTION TESTS ON ORIGINAL AMPOULES

After opening the original ampoule and transferring or using the solution, laboratories were asked to measure the activity remaining in the 'empty' original ampoule, after a defined washing procedure. The results are given in Table 6. After two washes with distilled water, between 0.05 - 0.3 % of the original activity was found to remain on the ampoules. Three

laboratories performed extra washings, and reported that the activity remaining dropped further, to 0.03 - 0.08 % of the original activity.

Table 5: Preliminary measurements of liquid masses and activity (at reference time 1998-07-01, 12h UT).

	BNM-LNHB	NPL`	PTB		CIEMAT	BIPM	NRCC	
Ampoule	A94/98	A114/98	A103/98		A97/98	A101/98	A99/98	A118/98
mass -total found in ampoule	-	4.04119g	4.05600(40)g		-	4.0424g	-	-
mass -according to distributing laboratory (IRMM)	4.07027(4)g	4.06023(4)g	4.05609(4)g		4.07274(4)g	4.05279(4)g	4.04815(4)g	4.06832(4)g
calibrated instrument	ion-chamber	ion-chamber	ion-chamber	Ge- gamma spectrometer	Ge- gamma spectrometer	ion-chamber	ion-chamber	
activity (kBq/g) -before opening original ampoule	151	147.03	149.7(0.8)	156(3)	140	149.2	144.5(1.2)	144.2(1.2)
date measured	1998-07-06	1998-05-20	1998-06-15 to 1998-06-19	1998-06-15 to 1998-06-19	1998-07-01	1998-06-12	1998-06-02	1998-06-02
activity (kBq/g) -after transfer to new ampoule	-	147.76	149.2(0.5) (to PTB ampoule)	148 (from drops weighed onto polyethylene foils)	140	-	-	-
date measured		1998-10-12	1998-06-29 to 1998-08-12		1998-07-01			

The values in the table include an uncertainty (in brackets) if given by the laboratory.

Table 6: Adsorption measurements after ampoule emptied and washed

	BNM-LNHB	NPL*	PTB*	CIEMAT	BIPM
measuring instrument	LS counter	ion-chamber	ion-chamber	Ge- gamma spectrometer	ion-chamber
activity left after two rinses with 5cm^3 distilled water & date of test	2000 Bq 1998-07-07	493 Bq 1998-09-22	1300(500) Bq 1998-06-30	300 Bq 1998-07-01	900 Bq 1998-06-30
activity left after an additional rinse & date of test	150 Bq 1998-07-07	-	-	200 Bq 1998-07-01	+2 rinses with 6M HCl 500 Bq 1998-06-30

The activities in the table include an uncertainty (in brackets) if given by the laboratory.
*PTB & NPL explicitly mention taking account of the residual activity in the ampoule when quoting their final result(s) for ^{237}Np activity.

11. PRIMARY ACTIVITY MEASUREMENTS

Primary activity measurements were made by six different techniques, as follows:

defined solid angle (BNM-LNHB, IRMM, PTB)

$4\pi(\alpha\beta)$-γ coincidence with efficiency extrapolation (NPL)

$4\pi\alpha$-γ coincidence at one efficiency (BNM-LNHB)

$4\pi\alpha$ counting (PTB)

$2\pi\alpha$ counting (CIEMAT)

liquid-scintillation by the NIST-CIEMAT method (PTB, CIEMAT)

The NRCC intended to perform $2\pi\alpha$ and $4\pi\alpha$-γ coincidence measurements, but was unable to do so because of source preparation difficulties.

11.1 HOW ‘ABSOLUTE’ ARE THE VARIOUS PRIMARY METHODS?

All measurements in this section are referred to as ‘primary’ measurements, although some of the methods may be considered to be more ‘absolute’ than others, dependent on the various assumptions adopted or the extent or significance of the nuclear data that was assumed. In principle an ‘absolute’ method should use as little information from other sources as possible. Of course, the various assumptions may well be justifiable, and each laboratory includes uncertainty assessments that aim to incorporate the uncertainty arising from such assumptions.

No criticism of the use of any of the methods is implied, and indeed it is most beneficial to the validity of the overall intercomparison that several different methods were used so that any systematic differences or effects of the assumptions in the methods may be revealed. Different laboratories will have varying views about the methods, and the brief comments in this section are merely those of the authors of this report.

The $4\pi(\alpha\beta)$-γ coincidence technique with efficiency extrapolation (NPL) would appear to be the most 'absolute' method, because no decay scheme parameters, except half-lives, are used. In addition, the efficiency extrapolation to 100% measured both ^{237}Np and ^{233}Pa emissions, but made no assumptions, except that the extrapolation was presumed to follow a smooth curve based on the data derived over a measurable range of efficiencies.

All other primary methods assume, albeit perhaps reasonably, that ^{237}Np decays by 100% alpha emission.

The BNM-LNHB coincidence method measured the ^{237}Np alpha emissions in a proportional counter, but required a major correction in the gamma channel to allow for ^{233}Pa gamma rays, which involves the assumption of various decay scheme parameters.

The $4\pi\alpha$ counting (PTB) method and the defined solid angle (PTB, IRMM, BNM-LNHB) method are both simple in principle, although corrections for source absorption and spectral tail extrapolation are required.

The CIEMAT-NIST method (PTB, CIEMAT) requires a sophisticated computer program which assumes a knowledge of many decay scheme parameters and uses a theoretical model with a tritium tracer as a basis to calculate the efficiency variation.

The $2\pi\alpha$ counting method (CIEMAT) appears to be the 'least absolute' of the primary methods, as it depends on significant theoretical corrections for backscatter and a spectral tail extrapolation.

11.2 DEFINED SOLID ANGLE METHOD (BNM-LNHB, IRMM, PTB)

Three laboratories measured the ^{237}Np activity by using a PIPS Si detector to measure alpha

particles emitted in a defined solid angle. The method assumes that every ^{237}Np decays by the emission of an alpha particle and that the intrinsic counting efficiency of the PIPS detector for the alpha particles is 100%.

LPRI dispensed sources from the original solution onto VYNS, whereas PTB dispensed sources at two dilutions onto stainless steel plates. IRMM prepared sources from the original solution and also from a 10 times dilution with 6M HCl, onto glass disks.

LPRI used a single fixed geometry, whereas IRMM and PTB used several fixed geometries.

The results and main components of uncertainty are given in Table 7.

Table 7: Defined solid angle method- activity results & uncertainties (1998-09-01, 12 h UT)

	BNM-LNHB	IRMM	PTB
^{237}Np activity kBq/g	150.2	149.6	149.30
combined uncertainty kBq/g	0.5	0.5	0.75
%	0.3 %	0.3%	0.50 %
dates of measurement	July 98-Feb 99	March 99-April 99	1998-07-21 to 1998-08-14
components of uncertainty	%	%	%
counting statistics	0.18	0.03 (typical)	0.25 (typical)
background subtraction		0.04	0.05 (typical)
weighing	<0.1	0.05	0.3 (between 0.1 & 0.34)
source preparation	0.1	0.01 (from dilution)	0.01 (from dilution factors)
deadtime		0.01	< 0.01 (count rates < 5 s^{-1})
pileup			< 0.01 (count rates < 5 s^{-1})
impurities		0.03	0.0
adsorption			≤0.05
self-absorption		≤0.03	≤0.1
geometry factor	0.25	0.15	0.30 (between 0.21 & 0.43)
detector efficiency		0.01	≤0.05
scattering at diaphragm & wall		0.01	0.1
back scattering at source support		0.01	-
extrapolation to zero volts	0.004	0.03	-
extrapolation to zero solid angle		0.03	-

The spread of the results from the three laboratories amounted to 0.6%, which is comparable with, if a little larger than, the estimated uncertainties of each laboratory.
Details of the equipment and samples used, with relevant parameters and calculation methods, are given in Table 8.

Table 8 :Equipment, sources and methods for defined solid angle measurements

	BNM-LNHB	IRMM	PTB
PIPS alpha detector:			
area of detector	1964 mm^2	3000 mm^2	600 mm^2
defining diaphragm		53.846 mm diameter	1 mm from detector
pressure		50 Pa	0.1 Pa
voltage		100V	50 volts
resolution	35 keV (@ 5 MeV)	55 keV (@ 5.5 MeV)	13keV(FWHM,@ 5.5 MeV)
source – detector	165.85 mm	5 mm	35; 50; 72 mm
solid angle	3.678E-3 sr	0.7 to 0.095 sr	0.06; 0,12; 0,24 sr
deadtime	9.5μs , non-extendable	live-time by precision gates. 20 μs	pulser method corrects for live-time and pile-up
discrimination level	2 volts	-	700 keV
number of geometries	one	several	three
Geometry factor		from dimensions by numerical integration	MonteCarlo method with system dimensions, source shape & density. The shape(a polygon) & density by autoradiography
Source preparation:			
from ampoule	A94/98	A119/98	A103/98
number of sources	3	15	6
diluted by	not diluted	some not diluted some 10x by 6M HCl	2 different dilutions. Both by 6M HCl & 20 (g/g oxalic acid.
weight of source	10 mg	10-50 mg	7.5 to 14 mg
source mount	Au-coated VYNS	glass disks	stainless steel plates
Spreading/seeding agent	latex microspheres (Tween20)	a drop of Ludox	silica gel
drying conditions	room temperature	hot gas jets	room temperature
final source covering	VYNS foil 0.3μ(m)	VYNS foil 24ug/cm^2	none
Storage		desiccator (hygroscopic)	room conditions
Spectrum extrapolation	to 0 volts	exponential extrapolation to zero energy, using data from 1.6-3.3 MeV (adds <0.05%)	no significant contributions of events below threshold
How is mean calculated		mean of all sources	unweighted mean of 10 measurements on 6 sources at 2 dilutions.

11.2.1 BNM-LNHB method:

Sources were prepared by dispensing 10mg drops from the original solution onto latex microspheres (Tween 20) on gold-coated VYNS foils, which were allowed to dry at room temperature and were then covered with 0.3 μm thick VYNS foils. The 50 mm diameter PIPS detector, which subtended 0.003678 sr at the source, had a resolution of 35 keV at 5 MeV. A threshold level of 2 volts was used, and the observed spectrum extrapolated to zero volts.

11.2.2 IRMM method:

Sources were prepared quantitatively from the original solution and a 10 times diluted one. Drying of the source drops was accelerated by a dry nitrogen gas flow at a temperature of 90°C while rotating the glass substrates *(Denecke, 1999)*, which resulted in nearly uniform deposits in a drying time of 3 minutes. The deposits were very hygroscopic, and therefore stored in desiccators.

The distance from a source to the defining 53.846 ± 0.005 mm diameter diaphragm was determined optically to ± 0.02 mm. The diaphragm could be placed at various well defined positions, resulting in solid angles from 0.7 to 0.095 sr.

It was assumed that large angle scattering at the glass substrate was less than 0.01%. Scattering at the diaphragm edge was calculated to be less than 0.01% *(Bambynek 1967)* and scattering on the chamber walls was insignificant due to thin baffles with knife-edges preventing α particles reaching the walls.

A live-timing method with precision live-time gates was used *(De Jonge 1980)* rather than the MCA live-time.

Background spectra were taken before and after each source measurement.

The alpha particles with an energy above 1.6 MeV were counted, and the counts from an exponential extrapolation to zero energy based on a fit between 1.6 and 3.3 MeV were added. This correction was 0.01 - 0.05% of the total count rate, dependent on source thickness. The standard deviation for all sources was 0.16%.

11.2.3 PTB method:

Sources were prepared at two dilutions (using 6M HCl with 20 μg/g oxalic acid) and dispensed onto stainless steel plates. The active area of the PIPS detector is defined by a circular diaphragm placed 1mm in front of the detector. Various spacers were used between source and detector to provide three different geometries. To determine the geometry factors, the radioactivity distributions of the sources were measured from autoradiographs using a storage phosphor screen: the shapes of such distributions are irregular and the maximum extensions varied between 7mm and 15mm. the distribution of each source was digitized and represented by a square matrix with a pixel size of 0.2 x0.2 mm^2. the numerical value of each pixel was taken proportional to the local activity at the source position represented by that pixel. The geometry factor was then calculated from the dimensions of the spectrometer and the radioactivity distribution of the source represented by the pixel matrix using the Monte Carlo method. The Monte-Carlo code has been checked for point sources and circular sources, for which the geometry factors can be calculated analytically by elliptical integrals.

11.3 COINCIDENCE METHODS (NPL, LPRI, [NRCC])

11.3.1 NPL method:

The NPL used a coincidence counting efficiency extrapolation technique with a 4π atmospheric pressure proportional counter (APPC) and a NaI detector, to obtain the sum of the ^{237}Np and ^{233}Pa activities (which were taken as equal). The method does not require a knowledge of any decay-scheme parameters.

The APPC was set at a voltage to include beta pulses from the ^{233}Pa as well as alpha pulses from the ^{237}Np and, in addition, conversion electrons and X-rays will be detected from both nuclides. The threshold of the amplifier, which follows the APPC, was set just above electronic noise. Two gamma channels were employed for 50-121 keV and 266-369 keV photons respectively (Figure 5). Measurements were made of the number of events in the proportional counter, N_{APPC}, and the number of coincidences, $Nc_{i,}$ between the APPC counts and the counts in each gamma channels, $N_{\gamma i}$, giving rise to two efficiency parameters $\varepsilon_i = Nc_i / N_{\gamma i}$. By repeatedly covering the sources with further VYNS films, a range of count rates were measured, enabling a 2-dimensional extrapolation of N_{APPC} in terms of the efficiency

parameters to give the total ^{237}Np + ^{233}Pa activity. The lower energy window, which includes about 12.3% of ^{237}Np decays and 2.0% of ^{233}Pa decays (as well as Compton events arising from higher energy gamma-rays), gave a maximum efficiency of 98.8% and exhibited an approximately quadratic efficiency dependence. The higher energy window, which includes the 300, 312 and 340 keV photopeaks from the β-decay of ^{233}Pa, but virtually no photons from ^{237}Np, gave a maximum efficiency of 93% and exhibited an approximately linear dependence. Altering the width of the lower energy window from 50-121 to 54-112 keV had no effect on the results.

The Cox-Isham/Smith formula *(ICRU 52, 1994)* was used to correct for non-extendable deadtimes and resolving times.

The total activity was derived from a least squares fit to

$$N_{APPC} = [\text{activity } ^{237}\text{Np} + \text{activity } ^{233}\text{Pa}] \; [\, 1 - k_{11}(1-\varepsilon_1) - k_{12}(1-\varepsilon_1)^2 - k_{21}(1-\varepsilon_2) \,],$$

where $\varepsilon_i = Nc_i / N\gamma_i$ for each gamma channel, and the k_{ij} are constants.

Preliminary measurements with sources made directly from the original solution resulted in relatively low efficiencies, and hence an accurate dilution (of 3.38814) was carried out to prepare higher efficiency sources. Tests of such diluted solutions using an ionization chamber (where the majority of the response arises from ^{233}Pa) showed that the ^{237}Np/^{233}Pa activity ratio remained in equilibrium. The diluted solution was weighed onto Au coated VYNS, and two unweighed drops of 6M HCl were added to spread each source. The sources were allowed to dry naturally in air at room temperature.

The extrapolation parameters (k_{ij} in the above equation) were derived from a least squares fit to data from two sources whose efficiencies were decreased by adding absorbing foils, as shown in Figures 6 & 7. These parameters were then applied to eight other similar sources which were measured at their maximum efficiency. Assuming secular equilibrium, the ^{237}Np activity is one half of the intercept represented by extrapolating to 100% in both of the measured efficiencies.

Corrections of -0.1% for radioactive impurities and +0.08% for ampoule adsorption were

made to give the final ^{237}Np activity value.

11.3.2 BNM-LNHB method:

The BNM-LNHB used a coincidence counting technique with a 4π atmospheric pressure proportional counter (APPC) and a Ge detector, to give the ^{237}Np activity. The APPC used a voltage suitable for detecting only alpha particles, and the efficiency of detection was based on measuring the coincidences (N_c) between the APPC counts (N_α) and photons detected by a Ge spectrometer in an 86.1 to 86.9 keV window ($N_\gamma^{observed}$).

The 86 keV window contained contributions from ^{237}Np and ^{233}Pa decays, and therefore the method requires a knowledge of the relative number of ^{237}Np ($\approx$12.3%) and ^{233}Pa ($\approx$2%) gamma-rays at this energy, so that the contribution of the ^{237}Np alone can be calculated. The method also assumes that no beta particles or conversion events (X-rays and electrons) were detected by the APPC.

It was assumed that [activity of ^{237}Np] $= \dfrac{N_\alpha}{\varepsilon_\alpha}$,

where $\varepsilon_\alpha = \dfrac{N_\gamma(^{237}\text{Np})}{N_c}$ and $N_\gamma(^{237}Np) = N_\gamma^{observed} \left\{ \dfrac{\dfrac{P^{Np}}{(1+\alpha_t^{Np})}}{\dfrac{P^{Np}}{(1+\alpha_t^{Np})} + \dfrac{P^{Pa}}{(1+\alpha_t^{Pa})}} \right\}$,

where P and α_t refer to the gamma emission probability and total internal conversion coefficient for the two 86 keV radiations. The values used were

$P^{Np} = 0.308 \pm 0.017$ $\alpha_t^{Np} = 1.5 \pm 0.1$ $P^{Pa} = 0.172 \pm 0.01$ $\alpha_t^{Pa} = 7.6 \pm 0.01$.

There is no efficiency extrapolation in this method: that is, in the equation

N_α = [activity of ^{237}Np] [$\varepsilon_\alpha + k\,(1 - \varepsilon_\alpha)$],

the gradient term, k, is assumed to be zero.

The sources used the original solution, and the weighed drops were deposited on latex

microspheres (Tween 20) onto Au coated VYNS, dried at room temperature and finally covered with VYNS.

A live-timing technique was used with an extendable deadtime common to the alpha and gamma channels.

The weighted mean of measurements on three sources was taken as the ^{237}Np activity.

11.3.3 NRCC method:

The NRCC intended to measure activity by a 4π alpha-gamma coincidence counting method, but suitable drop sources could not be prepared.

Attempts to produce sources by depositing 20-30mg drops of the original solution onto Au/Pd-covered VYNS films were not successful. The solution reacted with the coating, rendering the films non-conducting, and in addition the sources would not dry in air. Other sources were prepared on VYNS with catanac and dried in a vacuum desiccator, with the conducting layer being added later. However, it was difficult to say whether the source area was conducting.

When operating the gas-flow proportional counter in the alpha region, below that required for beta counting, NRCC considered that it was not possible to separate the alpha pulses from the X-rays, and commented that the observed count rate was approximately double that expected from ^{237}Np alpha particles alone.

Table 9 details the equipment and samples used, with relevant parameters and calculation methods. Results and the main components of uncertainty are listed in Table 10.

Table 9: Equipment, sources and methods for coincidence measurements

	NPL	BNM-LNHB	NRCC
Proportional counter and electronics:			
the counter	4π pill-box PC	4π pill-box PC	4π pill-box PC
diameter, height	75mm, 22mm : each half	100mm, 22mm : each half	
wall material	copper	perspex	
wire	Au-coated Molybdenum	Au-coated tungsten	
diameter, length	0.075mm, 75mm	0.020mm, 100mm	
voltage	2.1 kV	1.7 kV	
gas	A/CH4 at 0.1 MPa	CH4 at 0.1 MPa	
source - detector	13mm	10mm	
discrimination level	0.15 keV (above noise)	0.1 keV	
deadtime, μs	1.6 non-extendable	20.0 extendable, common	
resolving time, μs	0.75	1.0	
Gamma detector and electronics:			
the detector	one NaI(Tl)	one Ge, well type	
window	Al	carbon epoxy	
diameter, length	125mm, 95mm		
resolution	14.3% @ 312keV	<1.8keV@ 1330keV	
efficiency		15% at 1330keV	
distance to source	33mm	40mm	
energy window, keV	a) 50-121 or 54-112 b) 266-369	86.1-86.9	
deadtime, μs	2.0-2.5 non-extendable	20.0 extendable, common	
resolving time, μs	0.75	1.00	
Source preparation:			
from ampoule	A114/98	A94/98	A99/98
number of sources	10	3	
diluted by	3.38814x with 6M HCl	not diluted	not diluted
weight of source	18 mg approx	10 mg approx	20-30 mg
source mount	Au-coated VYNS	Au-coated VYNS	VYNS
spreading agent	2 drops HCl per source	latex microspheres (Tween20)	catanac
drying conditions	room temperature	room temperature	room temperature in vacuum desiccator
final source covering	none	covered with VYNS foil	add conducting layer
Efficiency variation	with extra VYNS foils	none	

Table 10: Coincidence measurements- activity results & uncertainties (1998-09-01, 12 h UT)

		NPL	BNM-LNHB	(NRCC)
^{237}Np activity	kBq/g	148.20	149.7	
combined uncertainty	kBq/g	0.83	2.0	
	%	0.56 %	1.2 %	
dates of measurement		mean date 1998-10-06	*July 98-Feb 99	
components of uncertainty		%	%	
counting statistics		0.12	0.7	
weighing		< 0.01	0.1	
deadtime		≤ 0.02	–	
pileup		≤ 0.01	–	
impurities		<0.01	–	
adsorption		0.2	–	
extrapolation of efficiency curve		0.14	n/a	
degree of fit used in extrapolation		0.48	n/a	
decay-scheme parameters		n/a	0.8	

*estimated as dates of receipt of ampoules and submission of results

11.4 $4\pi\alpha$ COUNTING METHOD (PTB)

PTB used a pill-box type atmospheric pressure proportional counter, with a discriminator set in the valley between the alpha and beta pulses to avoid counting events arising from ^{233}Pa decays (i.e. beta particles and conversion events). A change of counting gas from A/CH_4 (P10) to pure CH_4 had no effect on the results.

A total of 24 solid sources on VYNS were prepared, consisting of six from the original solution and six from each of three dilutions, with dilution factors of 5, 25, and 270. The method assumes every ^{237}Np decays by the emission of an alpha particle.

Significant corrections applied included:

a) Self-absorption in source material.

A plot of the activity per unit mass (of the original solution), as a function of $d^{-0.5}$, where d is the dilution factor, was assumed to be linear, and the intercept with the ordinate (i.e. at

infinite dilution) was considered to be the specific activity of the original solution corrected for self absorption (see Figure 8). Thus, sources at all strengths contribute to the final value, although the very dilute sources influence the extrapolation rather more than the strong sources. From the extrapolation, it may be deduced that the undiluted sources showed approximately 1.4% self-absorption.

b) Absorption in backing foil.

Foil absorption was determined from measurements using the upper and lower halves of the counter, and measurements with sources turned upside down. Further measurements were performed with additional absorber foils, ensuring such foils adhered closely to the first foil. For large dilution sources, a foil-absorption of 0.30(8)% was deduced.

c) Finite discrimination losses.

To avoid the measurement of beta particles and spurious pulses, a finite discrimination level was necessary. From a horizontal extrapolation of the pulse distribution to zero discrimination, a correction of 0.10(8)% was estimated.

d) Impurities.

^{238}Pu and ^{239}Pu impurities, amounting to 0.103(4)%, were identified from the alpha spectrometric measurements carried out at PTB.

Table 11 details the equipment, the samples and source preparation methods, with relevant parameters and calculation methods.

Results and the main components of uncertainty are listed in Table 12.

Table 11: Equipment, sources and methods for $4\pi\alpha$ counting (PTB)

	PTB
Proportional counter and electronics:	
the counter	4π pill-box PC
diameter, height	40mm, 22mm : each half
wall material	Al
wire	stainless steel and gold-coated molybdenum
diameter, length	0.040mm, 40 mm
voltage	2.7 kV with pure CH_4
gas	A/CH_4 or pure CH_4 at 0.1 MPa (result same for either gas)
source - detector distance	10mm
discrimination level	in valley between alphas and betas
deadtime, μs	5.005(5) not-extendable
background counts	0.06 s^{-1}
Source preparation:	
from ampoule	A103/98
number of sources	6 undiluted, 6 diluted 5.0291x, 6 diluted 25.0607x, 6 diluted 269.99x
diluent, where used	6M HCl and 20(g/g oxalic acid
weight of source	10-15 mg approx
source mount	On 15 $\mu g/cm^2$ VYNS, plated by Au/Pd both sides (2x 15$\mu g/cm^2$), and pretreated with colloidal SiO_2 by an electrospray device
spreading agent	2 drops HCl per source
drying conditions	oven dried at 40^{o}C
Absorption factors	
in source material	1.4%, determined from extrapolation to infinite dilution
in foil	0.30(8)% for most dilute sources, calculated from effects of : -upper/lower half count rates -upside down sources -effect of extra foils.
Spectrum extrapolation	A finite discrimination level was used to avoid counting beta particles. A horizontal extrapolation of pulse distribution to zero discrimination, gave 0.10(8) % correction.

Table 12: $4\pi\alpha$ counting- activity results & uncertainties (1998-09-01, 12 h UT)

		PTB
^{237}Np activity	kBq/g	149.14
combined uncertainty	kBq/g	0.34
	%	0.23 %
dates of measurement		1998-07-03 to 1998-08-07
components of uncertainty		%
counting statistics		0.1
weighing		0.12
deadtime		≤ 0.01
impurities		0.004
adsorption		≤0.05
self-absorption (from the extrapolation)		0.12
foil absorption		0.08
extrapolation to zero discrimination		0.08

11.5 $2\pi\alpha$ COUNTING METHOD (CIEMAT, [NRCC])

11.5.1 CIEMAT method

For the record, it should be noted that CIEMAT carried out these measurements in late-1999, after all other results were known from a first draft of this report. Earlier measurements by CIEMAT, submitted in 1998, have been withdrawn. These earlier data gave a low result of 138.18 kBq/g for the ^{237}Np activity. CIEMAT later attributed this low value to a faulty ADC. All sources prepared by CIEMAT were from ampoule A97/98, but it may be significant that the 1999 sources were diluted by factors of 19 or more, whereas the 1998 sources used the original strength solution.

CIEMAT prepared a total of 9 sources on 1 inch diameter Ag discs, each source deposit being between 20-30 mg. Five samples were also dispensed after the original solution was diluted by 19.0 μ factor of four after a 34.6545 times dilution (the diluent used was not specified.).

The $2\pi\alpha$ measurements were made with the following instruments, both of which used A/CH_4 (P10) counting gas:

a) 2π grid ionization chamber from Numelec, model NU14 B,
b) 2π large volume ionization chamber, CIEMAT design *(García Toraño 1997)*.

The method assumes that every ^{237}Np decays by the emission of an alpha particle.

Corrections were applied to allow for:

-backscattering according to the Crawford reference theory

-spectral tail extrapolation to zero energy

-impurities as measured by alpha spectrometry (see Table 2)

Concern was noted by CIEMAT that they had made a large number of transfers from ampoules to other ampoules and pycnometers between 1998 and their measurements in 1999, and that some evaporation may have effected their results.

The results and the main components of uncertainty are listed in Table 13.

Table 13: $2\pi\alpha$ counting- activity results & uncertainties (1998-09-01, 12 h UT)

	CIEMAT
^{237}Np activity kBq/g	150.2
combined uncertainty kBq/g	0.7
%	0.47 %
dates of measurement	1999-09-01
components of uncertainty	%
counting statistics	0.3
weighing	0.05
deadtime	0.02
impurities	0.02
adsorption	0.02
self-absorption	0.3
tail extrapolation & backscattering	0.2
possible evaporation after several liquid transfers between ampoules	(unknown)

11.5.2 NRCC

NRCC prepared sources from the original solution on stainless steel discs, but the solution reacted with the disks to form thick deposits. A source prepared on platinum showed no signs of a reaction but appeared to have a solid residue and was found to have an efficiency of only 88%. Measurements were unsuccessful and, therefore, no NRCC results were reported.

11.6 LIQUID SCINTILLATION USING CIEMAT-NIST METHOD (PTB, CIEMAT)

The CIEMAT-NIST liquid scintillation (LS) method *(García-Toraño 1988, Günther 1994)* was undertaken by PTB and CIEMAT, using tritium as a tracer. The technique gives the total activity of ^{237}Np plus ^{233}Pa. Both laboratories corrected for the presence of radioactive impurities.

11.6.1 PTB measurements

Fifteen LS sources were prepared, consisting of five from the original solution and five from each of two dilutions (5.0291 and 25.0607), using a diluent of 6M HCl with 20 μg/g oxalic acid. Each 20ml glass vial contained 10ml Ultima Gold AB with 1ml inactive diluent.
For ^{237}Np, the efficiency was assumed to be 100%, due to alpha emission and highly converted gammas. For ^{233}Pa, the efficiency was calculated using 17 decay paths with 5 betas and 11 converted gammas. The escape efficiency of a single decay path is the product of all escape efficiencies in the cascade.

The efficiency values of ^{237}Np/^{233}Pa are related to those of the tritium tracer (for the same free parameter, figure of merit, for the same quench), by a function approximated by a least squares fit

$$\varepsilon_{nuclide} = k_0 + k_1 \varepsilon_{tritium} + k_2 (\varepsilon_{tritium})^2 + k_3 (\varepsilon_{tritium})^3$$

as described by Günther *(Günther 1996).*

The total efficiency (for ^{237}Np + ^{233}Pa) was calculated to be 199.0%. All parameters used were taken from the database “NUCLEIDE”, the computerized form of Table de Radionucléides *(Lagoutine, 1987)* and from Be *(Be 1996 & 1998)*.

The measurements were performed during September 1998. A correction was applied for ^{237}Np/^{233}Pa dis-equilibrium, by following the count rates up to 37 days. At the start of measurements, the ^{233}Pa activity was only 99.5% of the Np^{237} activity.

Table 14: Liquid scintillation using NIST-CIEMAT method - activity results & uncertainties (1998-09-01, 12 h UT)

	PTB		CIEMAT	
^{237}Np activity	149.16 kBq/g		151.6 kBq/g	
combined uncertainty	0.37 kBq/g		0.8 kBq/g	
	0.25%		0.52%	
dates of measurement	1998-08-18 to 1998-09-25		1999-09-01	
components of uncertainty	%	remarks	%	remarks
counting statistics	<0.03		0.1	
weighing	<0.05		0.025	
deadtime	<0.03			
pileup	<0.03			
timing			0.01	
adsorption	0.10	from sample spread	0.02	
impurities	<0.03		0.02	
input parameters and statistical model	0.05			
quenching	0.11	0.05% from kB uncertainty. Estimated by processing with the parameter kB from 0.0060 to 0.0100 cm/MeV. 0.10% by using constants of (different) scintillator Hisafe2.	0.03	
interpolation from calibration curve	<0.03	0.7 % for tritium calibration curve		
decay-scheme parameters	0.11	0.11% from the 4% uncertainty of 527keV P_β with Eff=97.3%. 0.03% from M,N… Auger electrons.	0.06	
self absorption	<0.03			
extrapolation of efficiency curve	<0.03			
other effects	0.10	0.10% from ^{233}Pa adsorption during sample preparation.		
other effects			0.3	from tritium standard
other effects			0.4	state of equilibrium

Table 15: Equipment, sources & methods for LS counting by NIST-CIEMAT method

	PTB	CIEMAT
Liquid scintillation counter		
Type	Wallac Guardian 1414 (1996)	Wallac 1414 (1998)
Quench parameter	SQP(E)	SPQE / ^{152}Eu
Nuclide used as external standard	^{133}Ba	^{3}H
Efficiency with unquenched standard of ^{3}H	69%	60%
Background (unquenched standard in toluene scintillator, 0 to 2000+ keV)	53 min^{-1} (cpm)	1 s^{-1}
Options used (e.g. low-level counting)	None	
Samples (^{237}Np)		
Prepared from ampoule number	A103/98	A97/98
Number of sources at each dilution	5 undiluted, 5 at 5x, 5 at 25x	7 at 8x
Typical active drop masses, at each dilution	≈7mg, ≈35mg, ≈100mg	weight range not specified-editor
Chemical composition of samples	active weighed drop + 10ml Ultima Gold AB + 1ml diluent (6M HCl + 20μg/g oxalic acid)	active weighed drop + 15ml Hisafe III (no other additive mentioned)
Tracer (tritium)		
Standard used and origin	HTO standard, PTB	HTO standard, LPRI
Uncertainty of the standard (k=1)	0.33%	0.6%
Preparation date of tracer samples	1998-09-21	Jul/Aug 1999
Chemistry of tracer samples	Identical to Np samples	
Liquid scintillation parameters		
Numerical codes used	BEGA 98 and BM 98	
KB value	0.0090 cm/MeV	
Formula used to calculate ionization quenching correction factor Q/E	$Q = (k_1 + k_2 \log E + k_3 \log^2 E)/(1 + k_4 \log E + k_5 \log^2 E)$with constants of Hisafe2. the Los Arcos/Borras formula (*LosArcos 1990)*	
M, N,..X-ray and Auger electrons taken into account	No, only beta-gamma decay	
Model for interaction probability of photons with scintillator	Yes, roughly (alters ^{237}Np+^{233}Pa efficiency by ≈0.03%)	
Values used for cross section of interaction	MonteCarlo calculation, as in CIEMAT program EMI *(Grau Carles 1994)*	
	Calculation, as in CIEMAT EMI. Scintillator/6M HCl sample composition: H 9.7%, C 69.1%, N 0.1%, O 19.0%, Na 0%, P 0.1%, S 0%, Cl 2.0% and ρ = 0.96 g/cm^3	

The final result was derived as the unweighted mean of all results, which consisted of at least ten measurements for each of the fifteen sources. The results and the main components of uncertainty are listed in Table 14, and Table 15 details the equipment and samples used, with relevant parameters and calculation methods.

All nuclear data were taken from Table de Radionucléides *(Lagoutine, 1987),* sheet ^{237}Np and sheet ^{233}Pa.

11.6.2 CIEMAT measurements

(For the record, it should be noted that CIEMAT carried out these measurements in late-1999, after all other results were known from a first draft of this report.)

Seven LS sources were prepared, using a solution diluted by a factor of 7.9179 with HCl. Each low-background glass vial contained 15 ml HisafeIII. The stability of the sources was checked over a 3 week period.

12. SECONDARY ACTIVITY MEASUREMENTS WITH GAMMA SPECTROMETERS (BNM-LNHB, BIPM, NRCC)

Calibrated gamma-ray spectrometers were used by three laboratories to determine the ^{233}Pa activity, using the ^{233}Pa gamma-ray emission probabilities from the literature. The ^{237}Np activity was then assumed to equal the measured ^{233}Pa activity. In addition, NRCC measured the ^{237}Np activity from the 86 keV peak, making due allowance for the ^{233}Pa contribution.

The supplied glass ampoules were measured directly in the spectrometer by BIPM and NRCC. NRCC also measured thin solid sources by dispensing drops of the original solution onto a suitable mount. BNM-LNHB prepared five solid sources in a glove box, by weighing drops ($\approx$25 mg each) of the original solution onto mylar (18mm), which were dried at room temperature and covered with auto-adhesive scotch tape.

A typical photon spectrum is shown in Figure 3 and a typical efficiency calibration curve is

given in Figure 9.

The overall results based on the ^{233}Pa peaks are given in Table 16, along with the main components of uncertainty.

Table 16: Gamma spectrometry- activity results & uncertainties (1998-09-01, 12 h UT)

		BNM-LNHB	BIPM	NRCC
^{233}Pa activity	kBq/g	148.8	150.8	147.9
combined uncertainty	kBq/g	1.0	1.5	1.8
	%	0.7 %	0.99%	1.2 %
dates of measurement		*July 98-Feb 99	1998-06-22/23	June 98 - Sept 98
components of uncertainty		%	%	%
counting statistics		< 0.1	⎫	0.7
gamma-emission probabilities		0.6	⎪ 0.855	0.6
input parameters		0.2	⎪	0.3
extrapolation of efficiency curve		0.3	⎭	0.4
weighing		0.1	0.001	0.05
deadtime		≤ 0.02	0.1	<0.1
pileup		≤ 0.02	0.3%	<0.1
background		≤ 0.02	<0.1%	<0.1
self-absorption in solution		n/a	0.1	n/a
self-absorption in glass		n/a	0.35	n/a
e-γ/γ		0.1	N/A	n/a
source position		–	0.1	0.25

* estimated as dates of receipt of ampoules and submission of results

The results for each separately measured ^{233}Pa gamma line are given in Table 17 for ^{233}Pa. Each laboratory calculated a mean activity based on the weighted or unweighted mean, as indicated. In addition, the NRCC measured the ^{237}Np activity directly, based on the 86 keV peak, although the results (shown in Table 18) were rather low compared to all other activity results, and so these NRCC results in table 18 are not used further in this report.

Table 19 details the equipment and samples used, with relevant parameters and calculation methods.

Table 17: Gamma spectrometry- Measured ^{233}Pa activities and the assumed gamma emission probabilities for ^{233}Pa. (1998-09-01, 12 h UT)

	BNM-LNHB			BIPM			NRCC			
original ampoule	A94/98			A101/98			A99/98 & A118/98			
source type	5 solid sources			1 ampoule, as above			2 ampoules, as above			
E (keV)	P_γ	% uncert in P_γ	activity kBq/g	P_γ	% uncert in P_γ	activity kBq/g	P_γ	% uncert in P_γ	activity kBq/g	
									A99/98	A118/98
103.9	0.0086	3.49	150.5 (5.4)							
298.5 + 300.1	0.06655	1.0	148.8 (1.6)							
300							0.0662	-	148.0	146.9
312.0	0.3865	1.03	147.8 (1.6)				0.3865	-	147.0	147.7
340.5	0.045	1.11	148.4 (1.8)	0.0447	0.89	149.3 (1.8)	0.045	-	147.6	147.5
375.5	-	-	-	0.00679	1.2	153.7 (2.5)	0.0068	-	149.7	148.5
398.6	0.0141	1.42	148.5 (2.2)	0.01390	0.86	150.8 (1.8)	0.0141	-	147.1	146.7
415.8	0.0174	1.15	150.3 (1.8)				0.0174	-	148.9	149.5
P_γ from :	Table des Radionucleides (LPRI)			Nuclear Data Sheets *(Akovali 1990)*			Table des Radionucleides (LPRI)			
mean ^{233}Pa activity in original ampoule			148.8			150.8			148.0	147.8
how the mean was calculated	weighted mean of individual results from 5 sources and 6 gamma lines			weighted mean of results for 3 gamma lines, where results for each gamma line is weighted mean of several repeated measurements.			unweighted mean of 6 gamma lines			
uncertainty of mean	see table 16			see table 16			see table 16			

Table 18: Gamma spectrometry (NRCC) - ^{237}Np activity based on the measured 86 keV ^{237}Np gamma ray (1998-09-01, 12 h UT).

NRCC				
E (keV)	P_γ (^{237}Np)	^{237}Np activity (kBq/g)		
		ampoule A99/98	ampoule A118/98	5 thin sources from A99/98
86.5	0.123 assumed from the 'Table des Radionucléides' of LPRI.	129.9	129.8	143.0(3.0)
The observed 86.5 keV peak was adjusted for the presence of ^{233}Pa, by assuming its gamma-ray emission probability and the ^{233}Pa activity value.				
These results are included for completeness, but are not used further in this report. Note that the final NRCC estimate of ^{237}Np activity by gamma spectrometry is taken (as are the corresponding LPRI and BIPM activity estimates) from the activity of ^{233}Pa based on ^{233}Pa gamma lines.				

Table 19: Equipment and sources used in calibrated gamma spectrometry.

	BNM-LNHB	BIPM	NRCC	
source type	solid, from weighed 25 mg drops	the ampoule itself	the ampoules themselves	solid, from weighed drops
ampoule	A94/98	A101/98	A99 & A118/98	A99/98
number of sources used	5	1	2	5
solid angle	0.013 sr ($\cong$1% sr)	0.0063 sr	-	-
detector	Ge	Ge(Li)	Ge, extended range	Ge, extended range
well type?	no	no	no	no
diameter	54.6 mm	46 mm	56.5 mm	56.5 mm
volume	100 cm^3	60 cm^3	Rel.eff 20%	
material thickness	Be 0.5 mm	Al -	Be 0.5 mm	Be 0.5 mm
resolution: at 88 keV at 122 keV at 1332 keV	 - 0.66 keV 1.76 keV	 1.07 keV 1.08 keV 2.35 keV	 0.9 keV 1.8 keV 1.9 keV	 0.9 keV 1.8 keV 1.9 keV
source-detector distance	120 mm	500 mm	400 mm	100 mm
deadtime μs		51	4	4
corrections applied		a)dead-time b)pile-up c)self-attenuation in ampoule	nil n/a n/a	nil n/a n/a

A list of nuclides and gamma-ray energies used for efficiency calibration is given in Table 20 for BNM-LNHB and Table 21 for BIPM. No list of calibration nuclides was supplied by NRCC, although calibrated ampoules (containing 5ml liquid in 5ml BIPM type ampoules) were prepared from solutions standardized at NRCC by $4\pi\beta\gamma$ coincidence/anti-coincidence counting and from NIST standard reference materials, and for the solid sources, appropriate calibrated sources from NRCC and LPRI were used.

Table 20: BNM-LNHB- list of X- and gamma- rays used for Ge spectrometer efficiency calibration

Energy (keV)	nuclide		Energy (keV)	nuclide
5.0	^{51}Cr (KX)		136	^{57}Co
5.5	^{54}Mn (KX)		140	^{99m}Tc
6.0	^{55}Fe (KX)		166	^{139}Ce
6.5	^{57}Co (KX)		245	^{152}Eu
8.1	^{65}Zn (KX)		276	^{133}Ba
12 to 21	^{241}Am (XL)		296	^{192}Ir
13 & 15	^{85}Sr (KX)		296	^{152}Eu
14 & 16	^{88}Y (KX)		303	^{133}Ba
14	^{57}Co		308	^{192}Ir
22 & 25	^{109}Cd (KX)		320	^{51}Cr
26	^{241}Am		344	^{152}Eu
27 & 31	^{125}I (KX)		356	^{133}Ba
31 & 35	^{133}Ba (KX)		384	^{133}Ba
35	^{125}I		411 & 416	^{152}Eu
32 & 37	^{137}Cs (KX)		444	^{152}Eu
33 & 38	^{139}Ce (KX)		468	^{192}Ir
40 & 46	^{152}Eu (KX)		514	^{85}Sr
53	^{133}Ba		563 & 569	^{134}Cs
60	^{241}Am		603	^{124}Sb
79 & 81	^{133}Ba		604	^{192}Ir
88	^{109}Cd		605	^{134}Cs
122	^{152}Eu		662	^{137}Cs - ^{137m}Ba
122	^{57}Co			

(emission probabilities taken from Fischier LARA-LPRI, Saclay, France)

Table 21: BIPM- list of gamma- rays used for Ge spectrometer efficiency calibration

Energy	nuclide	Pγ	Reference
223.2	^{133}Ba	0.0045	NDS 49 (1986)
244.7	^{152}Eu	0.0753	IAEA - 619
276.4	^{133}Ba	0.07147	IAEA - 619
302.9	^{133}Ba	0.183	IAEA - 619
320.1	^{51}Cr	0.0986	IAEA - 619
356	^{133}Ba	0.6194	IAEA - 619
411.2	^{152}Eu	0.02356	Debertin Helmer & NDS 79 (1996)
444	^{152}Eu	0.03139	IAEA – 619 & NDS 79 (1996)

13. SUMMARY OF ACTIVITY RESULTS FROM ALL PARTICIPANTS

Table 22 lists the twelve separate results, noting the method and laboratory concerned, and gives an overall weighted and unweighted mean result. Two subgroups within Table 22 refer to the primary and secondary measurements separately, and the mean values are given for these two subgroups. The formulae used are given in the appendix.

Figure 10 shows the results graphically, along with the weighted mean results for the primary and the secondary measurements.

Nine primary standardizations were carried out by five laboratories (Table 22), using a range of methods, resulting in a total spread of 2.3% in the measured ^{237}Np activity. The weighted mean of the nine standardizations was 149.50 kBq/g with a standard uncertainty of 0.16%. The reduced χ^2 was 1.8, indicating that the scatter of the nine results was (only) a little larger than would be expected from the uncertainties supplied by each laboratory for the nine results.

The lowest activity concentration value (148.2 kBq/g) arose from the $4\pi(\alpha\beta)$–γ result of NPL and the highest value (151.6 kBq/g) arose from the liquid scintillation result of CIEMAT. The unweighted mean of the nine primary standardizations was 149.68 with a standard uncertainty of 0.21%. The difference between the weighted and unweighted means was only 0.12%.

Secondary standardizations, using calibrated gamma spectrometers, were performed by three laboratories (Table 22), resulting in broadly similar ^{237}Np activity estimates. The weighted mean of the three was 149.1 kBq/g with a standard uncertainty of 0.5%. The reduced χ^2 was 0.94, indicating that the scatter of the three results was very consistent with the uncertainties supplied by each laboratory for the three results.

The results of the primary and secondary measurements (149.50 and 149.1 kBq/g respectively) were consistent with each other : they differed by only 0.27%, whereas their standard uncertainties were 0.16% and 0.5% respectively.

The overall weighted mean result of all twelve measurements (i.e. both primary and secondary measurements in Table 22) was 149.48 kBq/g with a standard uncertainty of 0.14%. The reduced χ^2 was 1.50, indicating that the scatter of the twelve results was reasonably consistent with the uncertainties supplied by each laboratory for the twelve results.
The unweighted mean value of the twelve measurements was 149.55 kBq/g with a standard uncertainty of 0.20%, and differs by only 0.05% from the weighted mean value.

Table 23 groups the results according to the methods used and gives the mean result for each method. The table shows that there is no particularly significant difference, within the quoted uncertainties, between the results obtained by differing methods. The coincidence methods of NPL and BNM-LNHB are rather different, although they are grouped together in this table. The table also gives the weighted mean (149.48 kBq/g) of the five mean results of the five primary methods and the weighted mean (149.45 kBq/g) of all six methods, including the secondary method. As expected, these results are very similar to the corresponding weighted means in Table 22.

Table 24 is presented merely for academic interest. It groups the results of each laboratory together, giving the mean result for each laboratory, and the overall mean (149.38 kBq/g) of all the laboratories. This result is also very close to the mean value given in Table 22.

Table 22: Summary of the activity results. (998-09-01, 12 h UT)

Method / Lab	dates of measurements	activity kBq/g	uncert kBq/g	uncert %	
Primary measurements					
def.solid.angle / BNM-LNHB	*July 98 - Feb 99	150.2	0.5	0.3	
def.solid.angle / PTB	1998-07-21 to 1998-08-14	149.30	0.75	0.50	
def.solid.angle / IRMM	*July 98 - Apr 99	149.6	0.5	0.3	
$4\pi\alpha$-γ coinc / BNM-LNHB	*July 98 - Feb 99	149.7	2.0	1.3	
$4\pi(\alpha\beta)$-γ coinc / NPL	mean date 1998-10-06	148.20	0.83	0.56	
liquid.scint / PTB	Sept 1998	149.16	0.37	0.25	
liquid.scint / CIEMAT	mean date 1999-09-01	151.6	0.8	0.52	
$4\pi\alpha$ / PTB	1998-07-03 to 1998-08-07	149.14	0.34	0.23	
$2\pi\alpha$ / CIEMAT	mean date 1999-09-01	150.2	0.7	0.47	
weighted mean of 9 results above		149.50	0.24 [b]	0.16 [b]	. χ^2/df=1.8
unweighted mean of 9 results above		149.68	0.31	0.21	
Relative measurements					
γ-spect, ^{233}Pa / BNM-LNHB	**July 98 - Feb 99*	*148.8*	*1.0*	*0.7*	
γ-spect, ^{233}Pa / BIPM	*mean date 1998-06-23*	*150.8*	*1.5*	*1.0*	
γ-spect, ^{233}Pa / NRCC	**July 98 - Sept 98*	*147.9*	*1.7*	*1.2*	
weighted mean of 3 results above		*149.1*	*0.75* [a]	*0.50* [a]	*χ^2/df=0.94*
unweighted mean of 3 results above		*149.2*	*0.86*	*0.58*	
Primary & *relative* measurements taken together					
weighted mean of all 12 results above		149.48	0.21 [b]	0.14 [b]	χ^2/df=1.5
unweighted mean of all 12 results above		149.55	0.30	0.20	

* estimated as dates of receipt of ampoules and submission of results

[a] internal uncertainty (which exceeded the external uncertainty)

[b] external uncertainty (which exceeded the internal uncertainty)

$$\frac{\text{external uncertainty}}{\text{internal uncertainty}} = \sqrt{x^2/\text{df}}$$

Table 23: Summary of activity results, grouped for each method. (1998-09-01, 12 h UT)
Where a method was used by more than one laboratory, a mean value for the method is calculated.
(The coincidence methods of LPRI and NPL are grouped together in this table, although the methods were rather different.)

Method / Lab	dates of measurements	Activity kBq/g	Uncert kBq/g	Uncert %	activity kBq/g	uncert kBq/g	Uncert %	
Primary measurements								
def.solid.angle / BNM-LNHB	*July 98 - Feb 99	150.2	0.5	0.3	⎫			
def.solid.angle / PTB	1998-07-21 to 1998-08-14	149.30	0.75	0.50	⎬ weighted mean for solid angle method			
def.solid.angle / IRMM	*July 98 - Apr 99	149.6	0.5	0.3	⎭ 149.79	0.32[a]	0.21[a]	χ^2/df = 0.6
$4\pi\alpha$-γ coinc / BNM-LNHB	*July 98 - Feb 99	149.7	2.0	1.3	⎫			
$4\pi(\alpha\beta)$-γ coinc / NPL	mean date 1998-10-06	148.20	0.83	0.56	⎭ weighted mean for 'coincidence' methods 148.42	0.[77a]	0.51[a]	χ^2/df = 0.5
liquid.scint / PTB	Sept 1998	149.16	0.37	0.25	⎫			
liquid.scint / CIEMAT	mean date 1999-09-01	151.6	0.8	0.52	⎭ weighted mean for liquid scintillation 149.59	0.93[b]	0.62[b]	χ^2/df = 7.6
$4\pi\alpha$ / PTB	1998-07-03 to 1998-08-07				149.14	0.34	0.23	
$2\pi\alpha$ / CIEMAT	mean date 1999-09-01				150.2	0.7	0.47	
weighted mean for 5 methods above					149.48	0.23 [b]	0.15 [b]	χ^2/df=1.2
unweighted mean for 5 methods above					149.43	0.30	0.20	
Relative measurements								
γ-spect, ^{233}Pa / BNM-LNHB	**July 98 - Feb 99*	*148.8*	*1.0*	*0.7*	⎫			
γ-spect, ^{233}Pa / BIPM	*mean date 1998-06-23*	*150.8*	*1.5*	*1.0*	⎬ weighted mean for solid angle method			
γ-spect, ^{233}Pa / NRCC	**July 98 - Sept 98*	*147.9*	*1.7*	*1.2*	⎭ 149.1	0.75[a]	0.50[a]	χ^2/df = 0.94
Primary & *relative* measurements taken together								
weighted mean for 6 methods above					149.45	0.20 [b]	0.14 [b]	χ^2/df-1.03
unweighted mean for 6 methods above					149.37	0.25	0.17	

*estimated as dates of receipt of ampoules and submission of results
a internal uncertainty (which exceeded the external uncertainty)
b external uncertainty (which exceeded the internal uncertainty)

$$\frac{\text{external uncertainty}}{\text{internal uncertainty}} = \sqrt{x^2/\text{df}}$$

Table 24: Summary of activity results, grouped by laboratory. (1998-09-01, 12 h UT)
All results from a given laboratory are listed together, with an overall laboratory mean value.
The relative measurements by *gamma spectrometry are in italics.*

Lab / method	dates of measurements	activity kBq/g	uncert kBq/g	uncert %	activity kBq/g	uncert kBq/g	uncert %	
BNM-LNHB / def.solid.angle	*July 98 - Feb 99	150.2	0.5	0.3	⎫			
BNM-LNHB / 4πα-γ coinc	*July 98 - Feb 99	149.7	2.0	1.3	⎬ weighted mean for BNM-LNHB			
BNM-LNHB / γ-spect, ^{233}Pa	**July 98 - Feb 99*	*148.8*	*1.0*	*0.7*	⎭ 149.9	0.6[k]	0.4[k]	$\chi^2/df = 0.8$
PTB / def.solid.angle	1998-07-21 to 1998-08-14	149.30	0.75	0.50	⎫			
PTB / 4πα	1998-07-03 to 1998-08-07	149.14	0.34	0.23	⎬ weighted mean for PTB			
PTB / liquid.scint	Sept 1998	149.16	0.37	0.25	⎭ 149.16	0.24[a]	0.16[a]	$\chi^2/df = 0.02$
CIEMAT / liquid scint	mean date 1999-09-01	151.6	0.8	0.52	⎫ weighted mean for CIEMAT			
CIEMAT / 2πα	mean date 1999-09-01	150.2	0.7	0.47	⎭ 150.81	0.69[b]	0.46[b]	$\chi^2/df = 1.7$
IRMM / def.solid.angle	*July 98 - Apr 99				149.6	0.5	0.3	
NPL / 4π(αβ)-γ coinc	mean date 1998-10-06				148.20	0.83	0.56	
BIPM / γ-spect, ^{233}Pa	*mean date 1998-06-23*				*150.8*	*1.5*	*1.0*	
NRCC /γ-spect, ^{233}Pa	**July 98 - Sept 98*				*147.9*	*1.7*	*1.2*	
weighted mean of 7 laboratories					149.38	0.24[b]	0.16 [b]	$\chi^2/df = 1.63$
unweighted mean of 7 laboratories					149.48	0.43	0.29	

*estimated as dates of receipt of ampoules and submission of results

k takes account of fact that the same sources were measured in 2 of 3 BNM-LNHB methods

a internal uncertainty (which exceeded the external uncertainty)

b external uncertainty (which exceeded the internal uncertainty)

$$\frac{\text{external uncertainty}}{\text{internal uncertainty}} = \sqrt{x^2/\text{df}}$$

13.1 RECOMMENDED 'BEST' MEAN VALUES OF ACTIVITY CONCENTRATION

The weighted means in Table 22 are recommended as the 'best' available estimates of the ^{237}Np activity concentration. They are repeated here in Table 25.

Table 25: The 'best' mean values of ^{237}Np activity concentration (1998-09-01, 12 h UT). (data extracted from table 22)

Measurements	weighted mean	standard uncertainty
the 9 primary results	149.50 kBq/g	0.16%
the 3 secondary results (gamma spectrometry):	149.1 kBq/g	0.5%
the 9 primary and the 3 secondary results	149.48 kBq/g	0.14%

14. MEASUREMENT OF ABSOLUTE PHOTON EMISSION PROBABILITIES (PTB, NPL, BNM-LNHB/IFIN-HH)

Three participants, PTB, NPL, and BNM-LNHB/IFIN-HH, determined photon emission probabilities, P = R/activity, from the source emission rates R, which were measured with calibrated Ge, Ge(Li) or Si(Li) detectors, and from the activity, as measured by each laboratory.

Tables 26 and 27 list the calibration nuclides used and Table 28 summarizes the equipment and sources used. The measured emission probabilities are presented in Table 29 together with existing evaluated data *(Akovali 1990, IAEA 1986, Reich 1990)*. The various component contributions to the measured uncertainties are listed in Table 30.

The PTB reported a large number of X-ray and gamma-ray emissions based on separate measurements with several detectors. The BNM-LNHB/IFIN-HH reported on slightly fewer lines, using a planar and a coaxial Ge detector, with some measurements in coincidence. The NPL reported on 20 major gamma-rays based on measurements with one detector. The data reported here are taken from papers to be published at ICRM 1999 *(Schötzig 1999, Luca 1999, Woods 1999)*.

14.1 PTB MEASUREMENTS

The full-energy peak efficiency calibration curves for a Ge(Li) spectrometer (11 % relative efficiency), two HPGe spectrometers (25 % and 44 %) and a Si(Li) spectrometer used for the current measurements were obtained with activity-calibrated standard sources produced and measured at the PTB. The fitting of cubic spline functions to the efficiency calibration points resulted in standard uncertainties of at least 5 % below 10 keV, of about 1.5 % up to 80 keV, and 0.8 % from 80 keV to 1800 keV.

The number of counts in the gamma-ray peaks of the spectra was determined by fitting Gaussian and background functions, while the convolution of a Lorentzian with Gaussian and appropriate background functions were fitted to the X-ray peaks. Losses due to dead-time and pile-up effects were corrected using the pulser method *(Debertin 1997)*, while corrections for coincident summation were calculated by the computer program KORSUM for the various detector geometries *(Debertin 1979)*.

Measurements were carried out with one volume source (a glass ampoule with 2 ml of Np solution; activity about 300 kBq) and two point sources (aluminium ring carrying two polyester foils that enclose the active area of about 3 mm in diameter, produced by drying droplets of Np solution; activity about 10 kBq), especially used for the low energy region. One run consisted of six single measurements of 20 000 s to 100 000 s duration each, and up to 10 runs were performed with the four spectrometers used. Source-to-detector distances were about 18 cm for the Ge spectrometers and 6.5 cm for the Si(Li) spectrometer.

Measurements up to 21 keV were solely performed with the Si(Li) spectrometer. A double-pulse distribution at about 3 keV was assigned to the protactinium and uranium M X-ray radiations. The peak at 8.22 keV was corrected for an interfering Ta-L_α fluorescence line, because two Ta collimators are used between source and detector to avoid radiation scattered from the source foil and source holder giving rise to unwanted pulse distributions on the low energy side of the peaks. The region between 11 and 21 keV contains all Pa and U L-lines; the resolution of the detector was not sufficient to resolve all individual parts so, in some cases, the multiplet fitting yields emission probabilities only for groups of interfering peaks. A similar situation exists for the K X-ray region from 94 keV to 116 keV. From the measured peak area at 46.53 keV the counts of a background peak at the same energy had to be

subtracted.

On the whole the PTB measured emission probabilities confirm the evaluated data but have lower uncertainties. Three lines at 21.5 keV, 27.7 keV and 288.3 keV found by the spectrum fitting cannot be assigned to corresponding known transitions in the Np or Pa decay schemes. The results for the 258.46 keV and 279.65 keV gamma-ray transitions show unusually great deviations from the evaluated data which cannot be explained. The standard uncertainties given in parentheses include the uncertainty of the activity, of the detector efficiency and of the peak fitting.

14.2 NPL MEASUREMENTS

An intrinsic Ge detector was calibrated for gamma-ray detection efficiency and energy, using solutions which had been previously standardized at NPL. The original neptunium solution was diluted by a factor of 3.38814, to produce a stock solution from which aliquots were dispensed into 2 ml glass ampoules for the spectrometry. This stock solution was also used for activity measurements (section 11.3).

Measurements were undertaken with the 2 ml flame sealed ampoules placed 25 cm from the detector face, where any contribution from true summing was negligible. The "pulser" method was used to correct for dead-time and random summing effects *(Debertin and Helmer, 1988).* Efficiencies and their uncertainties at the energies corresponding to the main gamma-rays of ^{237}Np and ^{233}Pa were interpolated using a purpose written cubic-spline fitting routine.

Five ampoules of the ^{237}Np/^{233}Pa solution were each measured twice, resulting in the emission probabilities listed in Table 29. The uncertainties from the various components, listed in Table 30, were added in quadrature, with due allowance made for correlated data.

14.3 BNM-LNHB/IFIN-HH MEASUREMENTS

A planar Ge detector was used for energies below 150 keV and a coaxial Ge detector for higher energies. Calibration of the detectors was performed with standard sources as listed in Table 27. All the electronic equipment associated with the two detectors was conventional, including the pile-up rejection system.

Table 26: NPL- list of X- and gamma- rays used for Ge spectrometer efficiency calibration

Energy (keV)	nuclide		Energy (keV)	nuclide
26	^{241}Am		391	^{113}Sn
43	^{243}Am		514	^{85}Sr
60	^{241}Am		662	^{137}Cs- ^{137m}Ba
88	^{109}Cd		898	^{88}Y
122	^{57}Co		1173	^{60}Co
166	^{139}Ce		1332	^{60}Co
279	^{203}Hg		1836	^{88}Y
320	^{51}Cr			

(emission probabilities taken from *IAEA, TECDOC-619, 1991*)

Table 27: BNM-LNHB/IFIN-HH- list of X- and γ- rays used for Ge spectrometer efficiency calibration

Energy (keV)	nuclide		Energy (keV)	nuclide
5.0	^{51}Cr (KX)		140	^{99m}Tc
6.5	^{57}Co (KX)		166	^{139}Ce
13 & 15	^{85}Sr (KX)		201& 206	^{192}Ir
14	^{57}Co		245	^{152}Eu
22 & 25	^{109}Cd (KX)		276	^{133}Ba
26	^{241}Am		296	^{192}Ir
27 & 31	^{125}I (KX)		296	^{152}Eu
31 & 35	^{133}Ba(KX)		303	^{133}Ba
35	^{125}I		308	^{192}Ir
32 & 37	^{137}Cs (KX)		320	^{51}Cr
33 & 38	^{139}Ce (KX)		344	^{152}Eu
40 & 46	^{152}Eu (KX)		356	^{133}Ba
53	^{133}Ba		374	^{192}Ir
60	^{241}Am		384	^{133}Ba
81	^{133}Ba		411, 416 & 444	^{152}Eu
88	^{109}Cd		468	^{192}Ir
122	^{152}Eu		514	^{85}Sr
122	^{57}Co		589, 604 & 612	^{192}Ir
136	^{57}Co		662	^{137}Cs - ^{137m}Ba

(emission probabilities taken from Fischier LARA-LPRI, Saclay, France)

Five point sources prepared from the original neptunium solution, whose activity was taken from BNM-LNHB's two 'absolute' methods, i.e. defined solid angle counting (Section 11.2) and coincidence counting (Section 11.3), giving a weighted mean of (150.2 ± 0.5) kBq/g. Drops of about 25mg were dispensed onto mylar foils (6μm), air-dried and sealed with another mylar layer.

The equilibrium between ^{237}Np and ^{233}Pa in these sources was checked (as noted in Section 5 above) by using gamma spectrometry to measure the ratios of the 143 keV γ-ray to various ^{233}Pa γ-rays over a 14 week period. No significant change was observed, within the estimated uncertainty of 0.4%.

To reduce edge effects and obtain a flat energy response, a 0.2 cm thick tungsten collimator with a 1 cm circular opening was placed 1 cm in front of the planar detector, with the source at 8.4 cm from the Be window. For the coaxial detector, the sources were 12.0 cm from the Be window and measurements were made with or without a 0.01 cm tin absorber, which makes the response curve similar to a p-type detector and suppresses the coincidences with X-rays. The sources were measured for 250,000 seconds on each detector and a further set of measurements for 85,000 seconds was made on the coaxial detector with the tin absorber.

Single peaks were evaluated by a summation process. Multiplets were deconvoluted by the COLEGRAM code *(Ruellan et al 1995)*, which analyses gamma-rays by Gaussian functions with or without tailing terms and X-rays by Voigt functions, along with a background step function. Real summing effects were taken into account by the CORCO code *(Lépy et al 1986)*, giving a correction factor between 0.991 and 1.013 for the coaxial detector, and between 1.000 and 1.002 for the planar detector. Pile-up was negligible (<0.1%).

The unfolding of the ^{237}Np and ^{233}Pa peaks near 86 keV is difficult, as they differ in energy by only 0.3 keV. For this case, the COLEGRAM code was not used, but instead the ratio of the two peaks was found by comparing the direct and the coincidence mode registered spectra (i.e. in coincidence with an alpha particle detector, as noted in LPRI's method for absolute activity in Section 11.3). This gave the ratio 86.5 keV / (86.5+86.8) keV as 0.814 ± 0.016.

The emission probabilities listed in Table 29 are the weighted mean values of results from the different detector arrangements. The uncertainties from the various components, listed in Table 30, were added in quadrature. For the planar detector, the efficiency uncertainty was 0.7% at 30 keV and 0.4% at 150 keV. For the coaxial detector the efficiency uncertainty between 50 and 500 keV was 0.3-0.4%.

Table 28: Equipment and sources for absolute photon emission probabilities.

	PTB		NPL	BNM-LNHB/IFIN-HH	
source type	2ml glass ampoule (A123/98 &A103/98) two point sources between polyester foils, (from A103/98)		2 ml glass ampoules, by diluting 3.388x from A114/98.	Five point sources, from 20-30mg drops from A94/98, onto thin (6μm) mylar. Air dried & sealed with mylar foil	
approx ^{237}Np activity of sources	ampoule ≈ 300 kBq. foils ≈ 10 kBq		ampoules ≈ 90 kBq	foils ≈3100 to 4500 Bq	
Detector	Si(Li)	three Ge coaxial	Ge coaxial	Ge planar	Ge coaxial
relative efficiency at 1332 keV	Not defined	11, 25, 44%	20%		23.8%
diameter	16 mm	43; 51; 59 mm	49.5 mm (D)	-	54.6 mm
length	5mm	46; 63; 78 mm	54.6 mm (L)		
volume	1cm^3	67; 127; 212 cm^3	105 cm^3 (from D & L)	3.0 cm^2 x 1 cm	100 cm^3
wall material thickness dead layer	Be 0.05 mm 0.1μm Si	Al; Be; Be 0.5,0.5,0.5mm0 .4mm,0.3μm,0. 3μm	Be 0.5 mm 0.3 μm Ge	Be 58 μm 0.26 μm Ge	Be 0.5 mm 1.5 μm Ge
high voltage	-1500v	+2900; -2500, -2500 V	–3800 v	– 1800 V	– 3500 V
FWHM (keV) @ 5.9 keV @ 122 keV @1332 keV	 205cv - -	 -, 0.75;0.66 - - - 2.2;1.86;1.77	 0.688 - 1.65	 0.250 0.525 -	 0.493 0.662 1.78 k
FWTM/FWHM @1332 keV	 1.82	 1.94;1.86;1.85	1.85	<1.9	<1.85
pulse shaping constant (μs)	6	2; 4; 6	6	8	6
source-detector distance	≈ 65 mm	≈180 mm 160;185;190mm	250 mm	84 mm	120 mm

Table 29: Photon-emission probabilities in the decay of $^{237}Np \rightarrow {}^{233}Pa \rightarrow {}^{233}U$.
The table lists all gamma-ray transitions (Pa-γ and Np-γ) given in the decay schemes of Table of Isotopes (Firestone 1996).

		P_γ (with standard uncertainty in brackets, if known)					
E keV	Origin of radiation	*Akovali 1990* evaluation	*IAEA 1986* evaluation	*Reich 1990* evaluation	PTB	NPL	BNM-LNHB/ IFIN-HH
			(IAEA 261)	(priv. com)			
3.15	Pa-M	-			0.048(25)		
3.25	U-M	-			0.015(8)		
5.5	Np-γ	-			-		
6.68	Np-γ	-			-		
8.22	Np-γ	$\approx$0.090 $P_{\gamma+ce}$			0.0012(5)		
9.0	Np-γ	-			-		
10.7	Np-γ	-			-		
11.37	Pa-L_ℓ	-			0.0155(8)		
11.62	U-L_ℓ	-			0.0118(7)		
13.27	Pa-L_α	-			0.260(28)		
13.60	U-L_α	-			0.157(17)		
14.95	Pa-L_η	-			0.0064(6)		
15.4	Pa-$L_{\beta6;}$ U-$L_{\beta6}$, U-L_η	-			0.0066(5)		
16.0	Pa-$L_{\beta2,15}$, Pa-$L_{\beta4}$	-			0.0791(29)		
16.6	Pa-$L_{\beta1;}$ $L_{\beta5;}$U-$L_{\beta2,15}$, $L_{\beta4}$	-			0.274(11)		
17.2	Pa-$L_{\beta3;}$ U-$L_{\beta1}$,$L_{\beta3}$,$L_{\beta5}$	-			0.115(5)		
17.26	Pa-γ	$\approx$0.00004			-		
17.40	Np-γ	-			-		
19.50	Pa-$L_{\gamma1}$	-			0.0465(17)		
20.16	Pa-$L_{\gamma2}$,$L_{\gamma3}$,$L_{\gamma6;}$ U-$L_{\gamma1}$	-			0.0349(13)		
20.49	U-$L_{\gamma2}$	-			0.00806(29)		

		P_γ (with standard uncertainty in brackets, if known)					
E keV	Origin of radiation	*Akovali 1990* evaluation	*IAEA 1986* evaluation	*Reich 1990* evaluation	PTB	NPL	BNM-LNHB/ IFIN-HH
20.7	U-$L_{\gamma 3}$, U-$L_{\gamma 6}$	-			0.0103(4)		
21.5		-			0.00356(13)		
22.6	Np-γ	-			-		
24.14	Np-γ	-			-		
27.7		-			0.0084(7)		
28.38	Pa-γ	0.0011(4)	0.0015(1)		-	see text	0.00034(10)
29.37	Np-γ	0.150(10)	0.153(3)	0.153(3)	0.1412(15)	0.132(4)	0.1350(16)
28.38+ +29.37							0.1354(12)
29.6	Np-γ	-			-		
32.46	Np-γ	-			-		
36.24	Np-γ	-			-		
40.35	Pa-γ	0.00039(8)			-	0.000215(16)	0.00028(4)
41.65	Pa-γ	0.00013(4)			-		
43.2	Np-γ	-			-		
46.53	Np-γ	0.0011(1)	0.00106(6)	0.00110(4)	0.00104(4)	0.001067(19)	0.00150(5)
48.96	Np-γ	-			-		
51.5	Pa-γ	0.000004			-		
54.40	Np-γ	-			-		
57.1	Np-γ	0.0039(1)	0.00382(11)	0.0037(1)	0.00354(8)	0.00360(5)	0.00366(3)
57.90	Pa-γ	0.000009			-		
62.59	Np-γ	0.00006(3)			-		
63.90	Np-γ	0.00012(2)			-		
70.49	Np-γ	0.00012(3)			-		
74.54	Np-γ	0.00011(3)			-		
75.35	Pa-γ	0.0139(8)	0.0132(4)		0.0138(4)	0.01401(25)	0.01270(8)

		P_γ (with standard uncertainty in brackets, if known)					
E keV	Origin of radiation	*Akovali 1990* evaluation	*IAEA 1986* evaluation	*Reich 1990* evaluation	PTB	NPL	BNM-LNHB/ IFIN-HH
86.48	Np-γ	0.124(4)	0.123(2)	0.123(2)	see below	[0.1286(21) after assumed correction]	0.1140(24)
86.81	Pa-γ	0.0197(12)	0.0197(12)	-	See below	See below	0.0261(22)
86.48+86.81	Np-γ			0.142(3)	0.141(3)	0.1483(16)	0.1401(6)
87.99		0.0014(1)	0.00138(3)	0.00140(2)	-		0.00167(4)
86.48 to 87.99	Pa-γ						0.1417(6)
92.0	Pa-$K_{\alpha 2}$	< 0.00004			-		
92.28	Np-γ	0.0190(10)			0.0182(5)		
94.64	U-$K_{\alpha 2}$	0.006(2)			-		
94.65	Pa-$K_{\alpha 1}$	0.089(5)			0.0964(29)		
95.86	U-$K_{\alpha 1}$	0.0300(15)			0.0296(6)		
98.43	Pa-γ	0.145(8)			0.143(3)		
103.97	Np-γ	0.0087(3)	0.0087(3)		0.00840(17)	0.00853(8)	0.00856(5)
106.13	Np-γ	0.00053(5)			0.00046(40)		
107.6	Pa-$K_{\beta 3}$	0.0034(2)			0.00249(8)		
108.2	Pa-$K_{\beta 1}$	0.0069(4)			see below		
108.7	Np-γ	0.00068(15)			see below		
109.1	Pa-$K_{\beta 5}$,Np-γ?	-			see below		
108.2 to 109.1					0.00860(18)		
110.30	U-$K_{\beta 3}$	0.0180(9)			0.0189(4)		
111.4	Pa-$K_{\beta 2}$; Pa-$K_{O;P2,3}$;U-$K_{\beta 1}$	0.0365(16)			0.0382(8)		
114.9	U-$K_{\beta 2}$;U-$K_{\beta 4}$	-			0.0158(9)		
115.19	U-$K_{O;P2,3}$	-			0.00330(10)		
115.4	Np-γ	0.000026(8)			-		
117.70	Np-γ	0.0016(1)	0.00173(3)	0.00171(2)	0.00169(4)	0.00188(3)	

		P_γ (with standard uncertainty in brackets, if known)					
E keV	Origin of radiation	*Akovali 1990* evaluation	*IAEA 1986* evaluation	*Reich 1990* evaluation	PTB	NPL	BNM-LNHB/ IFIN-HH
131.10	Np-γ	0.00085(9)	0.00086(2)	0.00083(3)	0.000846(21)		0.00088(3)
134.28	Np-γ	0.00067(7)	0.00071(2)	0.00068(3)	0.000662(27)		0.00075(3)
139.9	Np-γ	≈ 0.00005			-		
141.74	Np-γ	-			-		
143.25	Np-γ	0.0043(2)	0.00432(8)	0.00431(8)	0.00438(7)	0.00439(5)	0.00428(3)
151.41	Np-γ	0.00232(12)	0.00234(4)	0.00237(4)	0.00230(24)	0.00228(3)	0.00244(3)
153.37	Np-γ	0.000050(10)			-		
153.6	Np-γ	-			-		
155.24	Np-γ	0.00092(9)	0.00092(2)	0.00086(4)	0.000882(18)		0.00091(6)
162.41	Np-γ	0.00032(4)			0.000325(12)		
162.50	Np-γ	-			-		
169.19	Np-γ	0.00073(7)	0.00071(1)	0.00071(1)	0.000633(19)		
170.59	Np-γ	0.00020(4)			-		
172.56	Np-γ	-			-		
176.12	Np-γ	0.00018(3)			0.00012(4)		
180.81	Np-γ	0.00020(4)			0.000157(10)		
186.9	Np-γ	0.00003(3)			-		
191.46	Np-γ	0.00025(4)			0.000191(12)		0.00015(4)
193.26	Np-γ	0.00049(5)			0.000437(10)		0.00030(5)
194.7	Np-γ	-			see below	see below	0.00033(8)
194.95	Np-γ	0.00184(10)	0.00185(2)	0.00185(2)	see below	see below	0.00163(7)
194.7+194.95					0.00177(5)	0.00161(4)	0.00196(6?)
196.86	Np-γ	0.00020(3)			0.000207(12)		0.00024(5)
191.4 to 196.86							0.00267(13)
199.95	Np-γ	0.00004(1)			-		
201.6	Np-γ	0.00044(5)			see below		

		P_γ (with standard uncertainty in brackets, if known)					
E keV	Origin of radiation	*Akovali 1990* evaluation	*IAEA 1986* evaluation	*Reich 1990* evaluation	PTB	NPL	BNM-LNHB/ IFIN-HH
202.0	Np-γ	-			see below		
201.6++202.0					0.000391(8)		
202.90	Np-γ	0.000048(19)			-		
209.19	Np-γ	0.00016(2)			0.000141(9)		0.00019(3)
212.29	Np-γ	0.00155(10)	0.00151(2)	0.00152(2)	0.00150(3)	0.00148(3)	0.00150(4)
214.01	Np-γ	0.00045(9)			0.000361(8)		0.00039(2)
212.3+214.0							0.00189(4)
219.8	Np-γ	-			-		
222.6	Np-γ	0.000020(10)			-		
229.9	Np-γ	0.00014(4)			-		
237.86	Np-γ	0.00063(7)	0.00059(1)	0.00059(1)	0.000567(6)		0.00056(3)
248.5	Pa-γ	0.00059(3)	0.00059(2)		see below	see below	0.00056(6)
248.90	Pa-γ	0.000050(14)			see below	see below	0.00006(3)
248.5++248.9					0.000616(10)	0.000607(12)	0.00063(6)
250.5	Np-γ	-			-		
257.09	Pa-γ	0.000064(14)			-		see below
257.30	Np-γ	-			-		see below
258.46	Pa-γ	0.000039(16)			0.000274(6)		see below
257.09 to 258.46							0.00036(5)
262.44	Np-γ	0.000068(14)			0.0000470(18)		
271.48	Pa-γ	0.00328(12)	0.0032(1)		0.00322(4)	0.00323(3)	0.00323(5)
279.65	Np-γ	0.00002(2)			0.000109(4)		
288.3		-			0.000164(5)		
298.89	Pa-γ	0.00035			-		0.0015(3)
300.34	Pa-γ	0.0662(6)	0.0663(6)		0.0655(7)	0.0666(6)	0.0639(6)
298.89+300.34							0.0654(7)

		P_γ (with standard uncertainty in brackets, if known)					
E keV	Origin of radiation	*Akovali 1990* evaluation	*IAEA 1986* evaluation	*Reich 1990* evaluation	PTB	NPL	BNM-LNHB/ IFIN-HH
312.17	Pa-γ	0.386(4)	0.386(4)		0.385(4)	0.387(4)	0.3780(23)
340.81	Pa-γ	0.0447(4)	0.0450(5)		0.0450(5)	0.0452(3)	0.0441(2)
375.45	Pa-γ	0.00679(8)	0.0068(1)		0.00686(7)	0.00690(6)	0.00687(6)
398.62	Pa-γ	0.01390(12)	0.0141(2)		0.01406(15)	0.01407(11)	0.01390(13)
415.76	Pa-γ	0.01745(16)	0.0174(2)		0.01765(18)	0.01771(14)	0.01740(7)

Table 30: Photon emission probabilities. Contributions to P_γ uncertainties. The combined uncertainty varies for each gamma line, but is based on the components listed below.

	PTB	NPL	BNM-LNHB/IFIN-HH
Dates of measurement	June - Aug 1998		
components of uncertainty	%	%	%
activity estimate	0.3	0.52	0.3
counting statistics	0.1 - 5	0.07 - 6.8	<0.1 (for a strong line)
weighing	0.1	0.03	
rate effects	0.1	0.25	
efficiency calibration	0.5 - 5	0.43 - 2.6	0.3 - 0.7
ampoule variation	<0.1	0.1	
single peak modelling	0.1	Assumed as part of "counting statistics" as reported	0.1
others (photon coincidence counting losses, pile-up, weighing)	0.1		<0.2
others (e.g. positioning)	<0.1	0.1	

14.4 COMMENTS ON MEASURED ^{237}Np GAMMA-RAY EMISSION PROBABILITIES

Good agreement has still not been obtained for all of the major γ-ray emission probabilities following the decay of ^{237}Np.

29 keV: The three experimental Euromet measurements are self-consistent, but differ from the evaluated value of Reich *(1990)* at the 1σ level, which suggests that the current evaluated value may be in error.

46 keV: The NPL value is consistent with the evaluated value, but the PTB and BNM-LNHB are significantly lower and higher respectively, than the evaluated value. No immediate explanation can be found, although it is noted that a correction is required for a non-negligible peak in the background at this energy.

57 keV: The NPL and BNM-LNHB values are in agreement with the evaluated value, but the PTB value is significantly lower. No immediate explanation can be found,

although it is noted that a correction is required for a weak γ-ray line following the decay of ^{233}Pa.

86 keV: This ^{237}Np γ-ray peak is troublesome to fit because ^{233}Pa has a γ-ray transition of almost identical energy. The total ^{237}Np + ^{233}Pa peak areas obtained by PTB and BNM-LNHB were consistent with the evaluated value, but the NPL value was significantly higher, by 4.4%.

The BNM-LNHB obtained spectra directly and in a coincidence mode (with an alpha detector) to obtain experimentally the ratio of ^{237}Np to ^{233}Pa peak areas, and hence was able to quote separate peak areas for each nuclide.

The NPL estimated the ^{237}Np γ-ray emission probability by theoretically compensating the measured peak area utilising other measured ^{233}Pa peak areas together with recommended emission probabilities: a value 4.5% higher than the evaluated value of Reich is found. Similarly, when the total ^{237}Np + ^{233}Pa peak area was considered, the NPL's measured value was 4.4% higher than the corresponding evaluated value. This would indicate that the NPL's estimate of the 86 keV ^{233}Pa γ-ray emission is consistent with its evaluated value, but that NPL's estimate of the 86 keV ^{237}Np γ-ray emission probability is inconsistent with its evaluated value. This is a major cause for concern as this emission is the one most often used for routine analysis and is, indeed, the basis for all normalisation of relative emission probabilities.

117 keV: The NPL value differs significantly from both the PTB and the evaluated value. NPL surmised that fitting problems may be to blame, with this peak positioned within a portion of the spectrum where the Compton background is playing a major role (see, for instance, *Woods (1988)*).

195 keV: All three experimental values and the evaluated *(Reich 1990)* value differ significantly from each other. This line is a doublet, and NPL expressed concern about the quality of fit obtained using commercial fitting software. The PTB and NPL values are lower and the BNM-LNHB value is higher than the evaluated value.

279 keV: This line was measured only by PTB, whose result showed an unusually great

deviation from the current evaluated data.

143/151/212 keV: Reasonable agreement was observed between PTB,NPL,BNM-LNHB and the existing evaluated values.

14.5 COMMENTS ON MEASURED ^{233}Pa GAMMA-RAY EMISSION PROBABILITIES

28 keV: Only BNM-LNHB quoted a result, which differed greatly from the current evaluated values. NPL was unable to obtain an adequate fit to the peak and PTB did not quote a result. It is a very difficult peak to analyse in that it comprises the weak emission in a doublet with a transition following the decay of ^{237}Np.

40 keV: The NPL and BNM-LNHB values are (just) consistent, but differ significantly from the Reich evaluated value. The PTB did not quote a value.

75 keV: The BNM-LNHB value is significantly lower than both the NPL and PTB values, with Reich's evaluated data being midway. It is probable that interference from Compton γ-rays and Pb X-rays are significant, making deconvolution and accurate peak fitting difficult, particularly with commercial software.

86 keV: The BNM-LNHB value for the ^{233}Pa component of this peak is significantly higher than the evaluated values. The BNM-LNHB obtained its value from direct and coincidence spectra (see Section 14.3). The NPL and PTB did not obtain an experimental value.

258 keV: This line was measured only by PTB, whose result showed an unusually great deviation from the current evaluated data.

298.89 and 300.34 keV: The NPL and PTB values were consistent with the evaluated values, but the BNM-LNHB values were significantly different.

All other γ-ray transitions following the decay of ^{233}Pa, that were measured by two or more laboratories, were in satisfactory agreement and were approximately consistent

with existing evaluated values.

14.6 FINAL COMMENTS ON PHOTON EMISSION MEASUREMENTS

A number of results are tabulated in Table 29 where there appears to be an inconsistency either in the measured results or between those results and the earlier evaluated data.

The γ-ray emission probabilities following the decay of ^{237}Np continue to be of major concern. Self-consistent agreement as to their best values has not been obtained. However, within the work currently undertaken, a value for the 29 keV transition probability lower than that accepted at present is indicated. This may be of importance in the continuing attempts to balance the decay scheme of ^{237}Np as this transition, as can be seen from Figure 1, is pivotal in attaining a reliable scheme.

The NPL commented that with the availability of well characterised, standardized solutions, further work could usefully be done to try to resolve the problems still inherent within this decay scheme. Particularly, further studies of the γ-ray emission probabilities could be undertaken and complemented, if possible, with new studies of the internal conversion following the decay of ^{237}Np (as recommended by *Woods et al (1988)* and *Pearcey et al (1990)*).

15. DETERMINATION OF ^{237}Np ABSOLUTE ALPHA EMISSION PROBABILITIES (IRMM)

The IRMM work reported in this section is based on the paper of Sibbens *(Sibbens, 1999),* which reported alpha emission probabilities for 20 transitions.
Measurements on the decay scheme of ^{237}Np data were performed at IRMM in 1984 *(Vaninbroukx 1984)* and in 1990 *(Bortels et al., 1990)* using a source prepared by vacuum deposition on a quartz disc in 1983. After improvements of the detector and the electron deflection system, new measurements were started in 1998, using the same source from 1983. This source has a $^{237}NpF_4$ layer of 8 mm diameter at about 5μg/cm^2 superficial density. An impurity of only 0.1% ^{238}Pu was found by α-particle spectrometry.

An important requirement for the deconvolution of the complex α-particle energy distribution is the absence of coincidences between the α particles and the conversion

electrons resulting from the prompt transitions of the excited levels in the decay of the daughter nuclide ^{233}Pa. This was achieved by creating a strong magnetic field between the source and the detector, which ensured that the electrons emitted from the source towards the detector were deflected and could not reach the detector. Complete suppression of coincident conversion electrons up to 190 keV was verified by comparing the electron energy distribution below 400 keV with and without the magnetic field.

The detector subtended a solid angle of 0.113 sr at the source, although the magnet and diaphragm reduced this to 0.102 sr (Figure 11).

The spectra were taken with a 50 mm^2 high resolution PIPS detector having an entrance window of less than 20 nm. thickness. The detector and preamplifier were stabilised at 19.5 °C by a thermostatic bath. A total of 145 spectra (6 hours each) were recorded and were fitted to check for linear drift and shifted by up to two channels, if necessary. The spectra were summed together and corrected for background, resulting in one spectrum suitable for analysis using the computer code ALFA *(Babeliowsky 1993)*. ^{233}U was used for energy calibration.

The deconvolution was performed for the energy region from 4494 keV to 4885 keV, by dividing it into two windows, below and above 4700 keV. In the upper window, which contains the three major ^{237}Np peaks, the peak-shape parameters were optimized. For each peak the area and position were optimised individually in both windows using the same shape parameters. An initial fit starting with the previously known 14 α-particle peaks left a pattern in the residuals (see (b) in Figure 12) which revealed the probable presence of 6 extra peaks. By introducing these peaks into the fitting process, the residual pattern was improved (see (a) in Figure 12). A total of 20 α-particle transitions with a FWHM of 9.28 keV could be identified (Figure 12), including five transitions not found in the adopted ^{237}Np decay scheme *(Firestone 1996)*. .

The α-particle emission rate was derived from the same spectrum by taking the integral between 1090 keV and 4886 keV. The cut-off energy of 1090 keV was chosen to separate the α-particle spectrum from the β-ray spectrum of ^{233}Pa. The tail cut-off correction of 0.14% was obtained as an exponential extrapolation of the low tail of the spectrum to zero energy. The parameters used for the calculation were taken from an exponential fit of the flat part of

the low-energy tail in the region between 1090 and 2300 keV. The low-energy tail contributed only 1.4% of the total spectrum. The tail is subtracted prior to the peak analysis.

Table 31 Absolute alpha-particle emission probabilities of ^{237}Np

This work		*Bortels 1990*		*Firestone 1996*	
E_α	P_α	E_α	P_α	E_α	P_α
(keV)		(keV)		(keV)	
4515.1(19)	0.00035(4)	4513.7	0.00041(4)	4514.5(20)	0.0004(2)
4550.5(22)[a]	0.00011(3)				
4572.6(26)	0.00048(23)			4572.1	
				4573.8(20)	0.00054
4578.6(14)	0.00369(23)	4577.5	0.0041(2)	4581.0(20)	0.0040(4)
4599.1(18)	0.00371(9)	4598.5	0.0039(2)	4598.6(20)	0.0034(4)
4619.7(21)[a]	0.00032(8)	4619		4620.0	
4640.0(10)	0.0643(3)	4639.5	0.0645(4)	4639.4(20)	0.0618(12)
4665.0(9)	0.03478(24)	4664.6	0.0343(4)	4664.0(20)	0.0332(10)
4680.5(18)[a]	0.00020(4)				
4698.2(8)	0.00535(10)	4698.0	0.0054(4)	4694.4(20)	0.0048(20)
				4708.3(20)	
4710.8(7)	0.01174(13)	4710.6	0.0120(5)		
				4712.3(20)	
		4748		4741.3(20)	0.00019
4766.5(8)	0.0932(29)	4766.4	0.097(3)	4766.0(15)	0.08(3)
4771.4(8)	0.2315(29)	4771.4	0.2265(40)	4771.0(15)	0.25(6)
4788.0(9)	0.4764(6)	4788.1	0.4775(20)	4788.0(15)	0.47(9)
4803.5(10)	0.02014(17)	4803.6	0.0206(5)	4803.3(20)	0.0156
4816.8(10)	0.02430(17)	4817.0	0.0247(2)	4817.3(20)	0.025(4)
4824.5(36)[a]	0.00014(11)				
4848.9(49)[a]	0.00006(4)				
4866.4(14)	0.0053(4)	4866.4	0.0049(3)	4862.8(20)	0.0024
4872.7(14)	0.0239(4)	4873.0	0.00243(3)	4873.0(20)	0.0044

[a] The newly found transitions.

The method assumes every ^{237}Np decays by the emission of an alpha particle, so that a normalisation can be made to obtain absolute emission probabilities, by requiring that the sum of the 20 alpha emission probabilities must be unity. Results for the absolute α-particle emission probabilities of ^{237}Np are given in Table 31. Table 32 details the equipment, source and method. The uncertainties corresponding to one standard deviation are determined by

calculating covariance matrices *(Sibbens 1998)*. The quoted energy levels of ^{233}Pa were calculated from the difference between the given decay energy, the Q_α = (4957.3 ± 1.1) keV *(Lagoutine 1987)* and the α-particle transition energies, $E_{T\alpha} = E_\alpha(1+M_\alpha/M_R)$ using the atomic masses of the alpha and recoil atom. The Table 31 also lists the earlier results of Bortels *(Bortels 1990)* and the data from Firestone *(Firestone 1996)*.

It should be noted that these alpha emission measurements did not use the neptunium solution prepared for the Euromet 416 project but a source prepared by vacuum deposition on a quartz disc in 1983. The activity of this source, used for the determination of the ^{237}Np alpha-particle emission probabilities, is measured by alpha-particle counting at a defined low solid angle. This primary method is also used for the standardization of the ^{237}Np solution used in the Euromet 416 project and links the results to the BIPM reference activity value.

Table 32: Summary of equipment, source and method for α-particle spectra (IRMM).

	IRMM
PIPS alpha detector:	
type	thin window
area of detector	50 mm^2
resolution	9.28 keV
diaphragm	partly defines the solid angle (in conjunction with magnet)
Special features	
bending magnet	magnetic field stops conversion electrons reaching detector
temperature stabilisation	detector & preamp in thermostatic bath at 19.5°C.
Source:	
origin	thin layer of $^{237}NpF_4$ on a quartz disc, prepared in 1983 by vacuum deposition
active area	8mm diameter, 5μg/cm^2 thick
solid angle	detection system subtends ≈ 0.102 sr at the source
Spectral analysis	
region counted	1090-4884 keV
low energy tail correction	add 0.14% for tail cut off below 1090 keV, based on an exponential fit between 1090-2300 keV.
total tail area	the whole tail area was only 1.4% of total spectrum : this tail is subtracted prior to analysis
peak fitting	fit 20 alpha peaks in region 4494-4885 keV
impurity	0.1% ^{238}Pu impurity in this material from 1983, but the

	^{238}Pu peaks do not interfere with ^{237}Np peaks

16. CONCLUSIONS

This Euromet project has stimulated a wide range of measurements of ^{237}Np and ^{233}Pa. The ^{237}Np activity was measured in nine primary standardizations by five laboratories, using a wide range of methods which resulted in a weighted mean of 149.50 kBq/g with a standard uncertainty of 0.16%. The total spread in the results amounted to 2.3%.

Secondary standardizations, using calibrated gamma spectrometers, were performed by three laboratories, resulting in a weighted mean of 149.1 kBq/g with a standard uncertainty of 0.5%.

Three participants determined ^{237}Np and ^{233}Pa absolute photon emission probabilities. The results for most of the emissions were self-consistent between the three participants and with earlier evaluated data, but there were several important emissions where inconsistencies remain. The inconsistencies were found in the following emissions:

^{237}Np: 29, 46, 57, 86, 117, 195, 279 keV

^{233}Pa: 28, 40, 75, 86, 258, 300 keV.

One participant, IRMM, determined absolute emission probabilities for twenty α-particle transitions, giving results with a significantly lower uncertainty than achieved in earlier work. Five of the twenty corresponded to newly found transitions, not in the presently adopted decay scheme of ^{237}Np *(Firestone et al 1996).*

At the time of writing this preliminary report, no laboratory has reported mass concentration values, so that the intention noted in Section 1(g), to determine a new value for the half-life, is the only significant part of the project that has not been achieved.

ACKNOWLEDGMENTS

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form and especially to those who submitted supplementary information.

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Figure 1: The decay scheme of ^{233}Pa (from CEA/LPRI Table des Radionucléides)

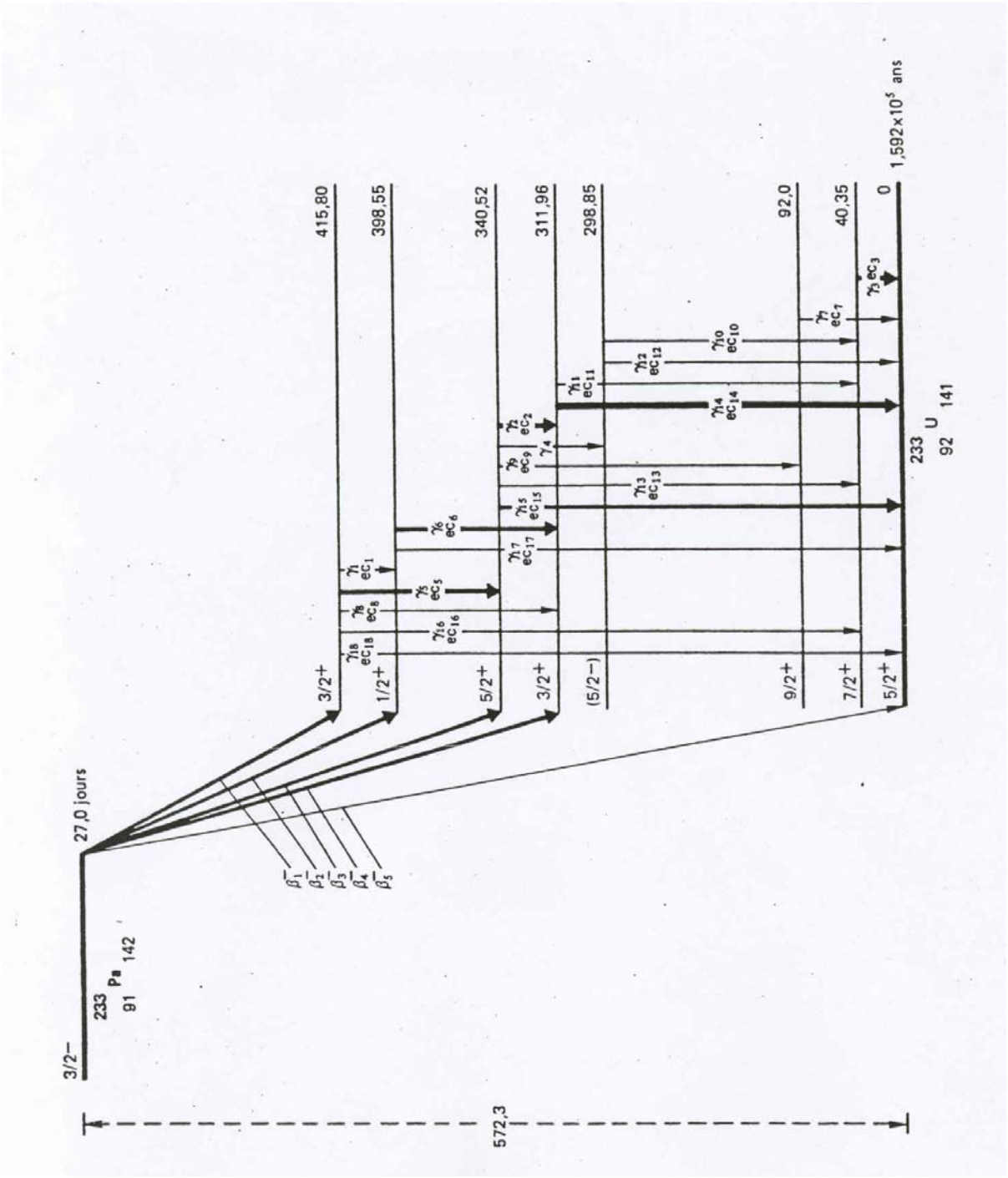


Figure 2: The decay scheme of ^{237}Np (from CEA/LPRI Table des Radionucléides)

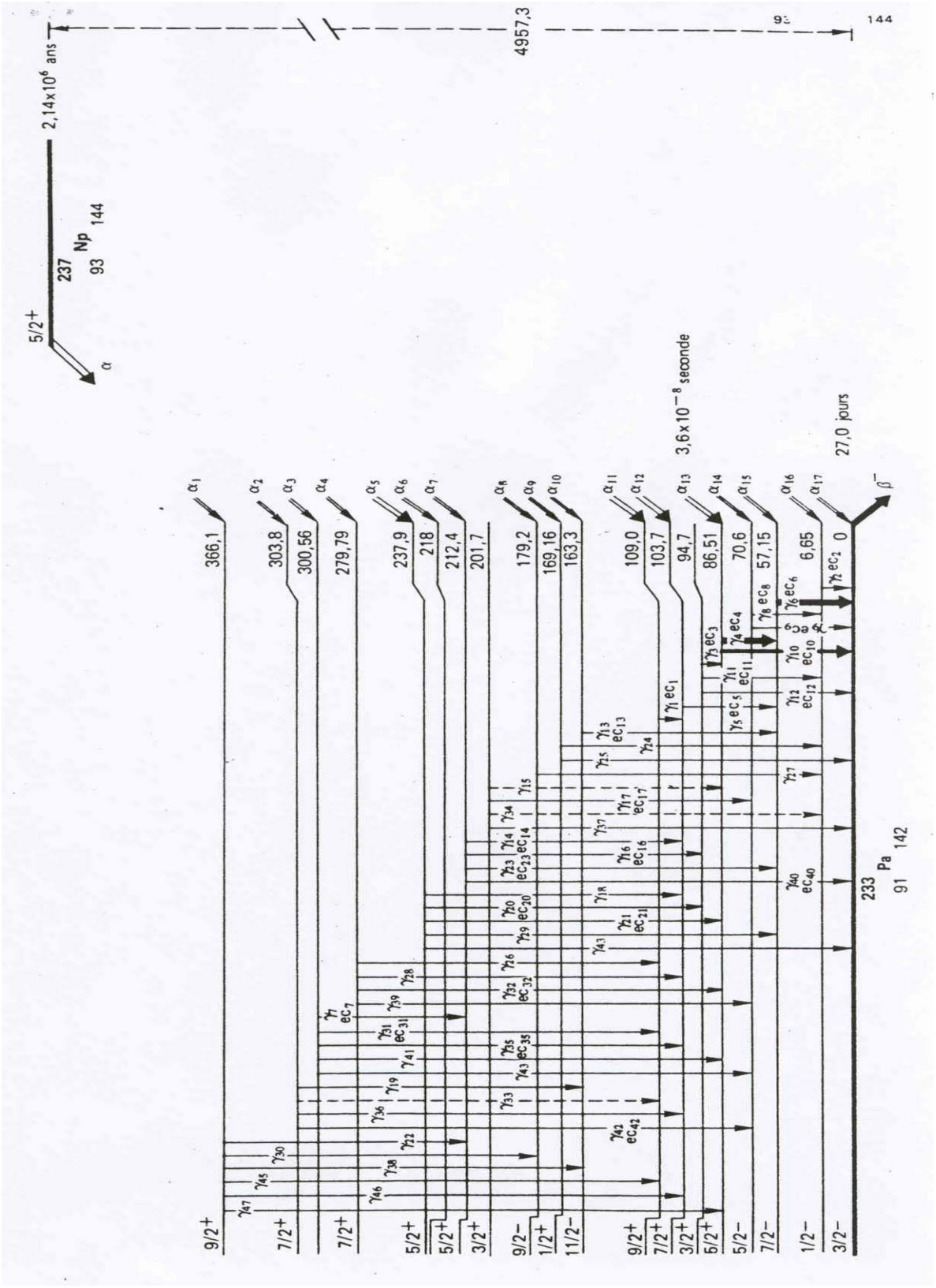


Figure 3: Spectrum from an ampoule of $^{237}Np/^{233}Pa$, recorded on a germanium detector (NRCC).

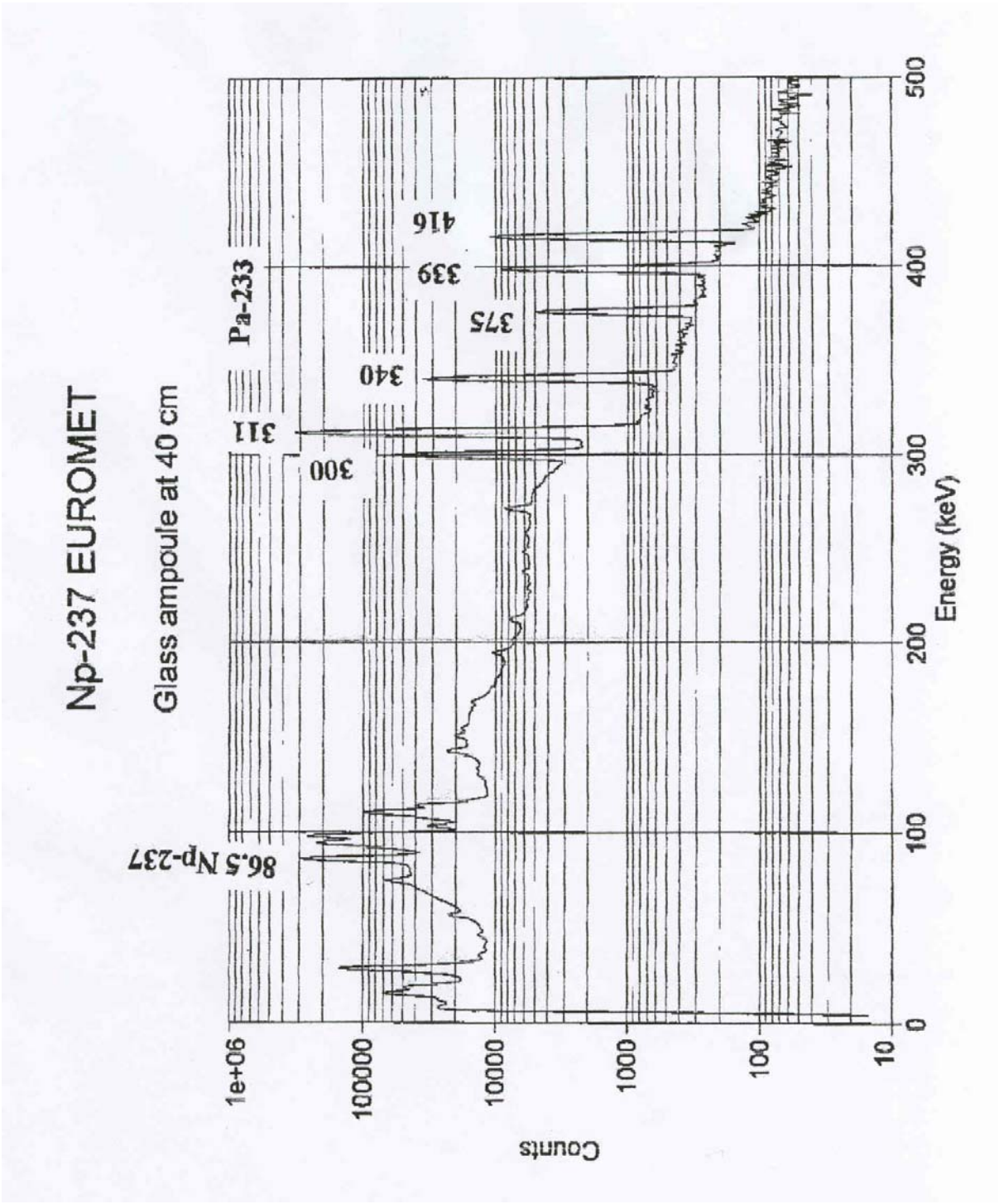


Figure 4: Impurity measurement (PTB) Spectrum of a ^{237}Np source in an alpha spectrometer. Impurities can be seen above 5 MeV.

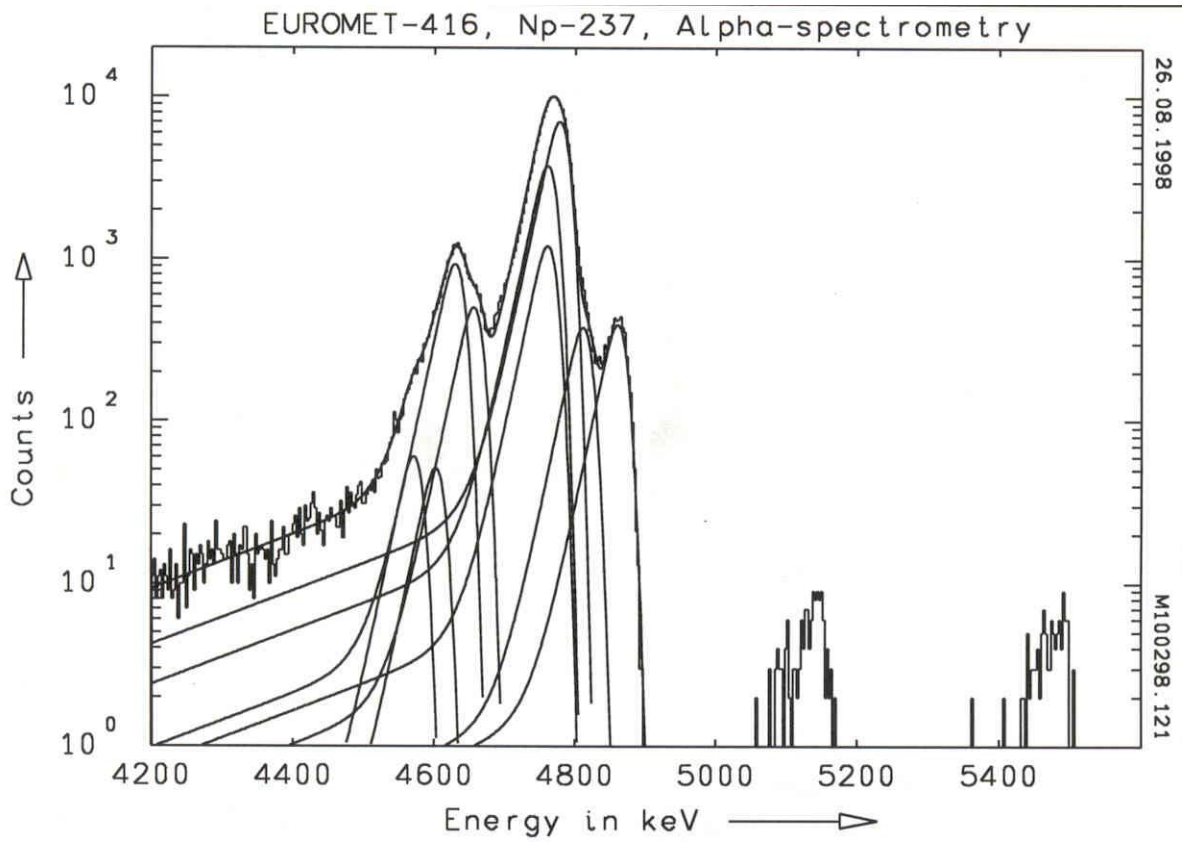


Figure 5: $4\pi(\alpha\beta)$-γ method (NPL).Gamma-ray spectrum from NaI detector, with the two gamma windows used.

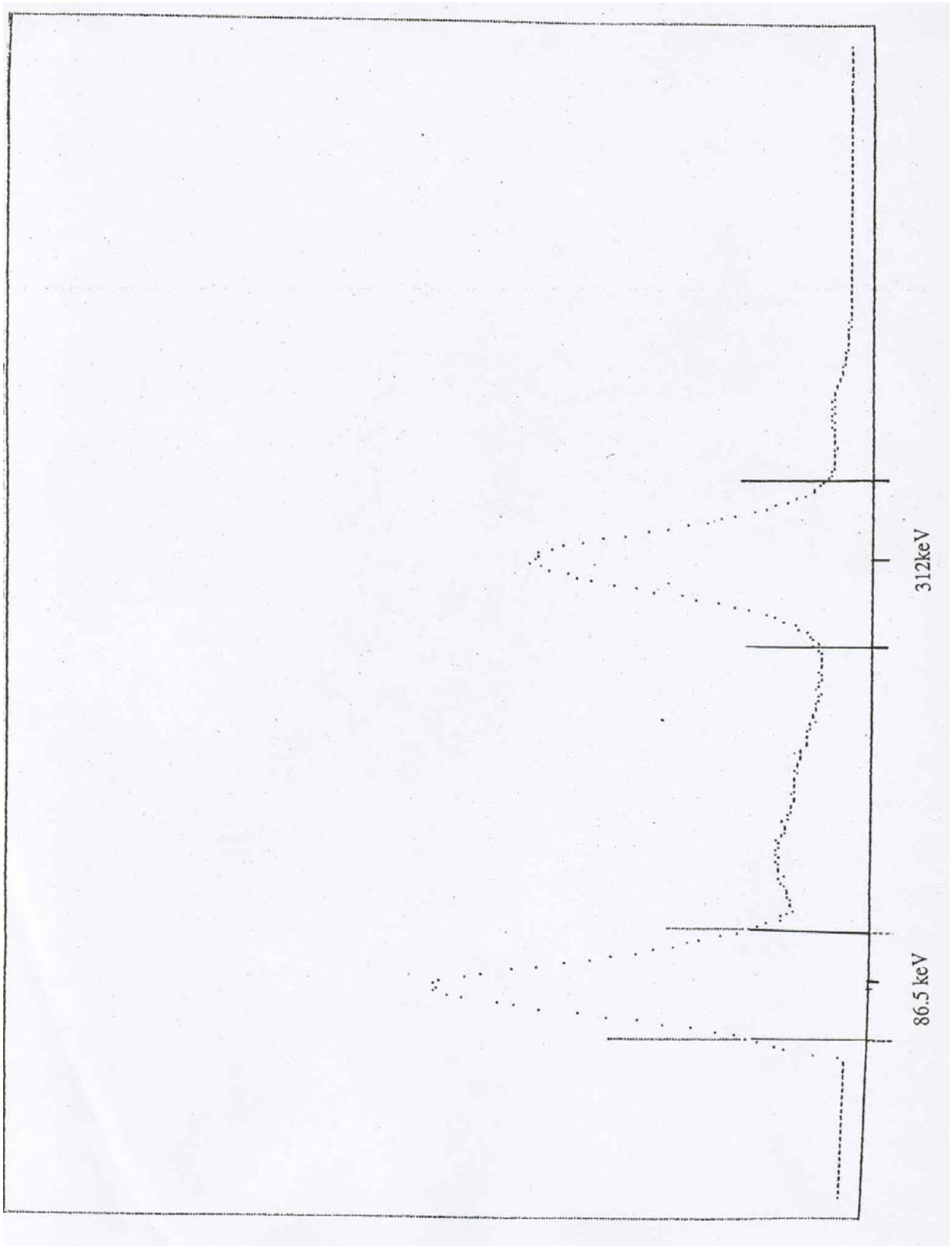


Figure 6: **$4\pi(\alpha\beta)$-γ method (NPL).Two-dimensional efficiency extrapolation, showing one aspect of the fit. Another aspect of the same fit is shown in figure 7. The abscissa is $(1-\varepsilon_2)$ where $\varepsilon_2 = Nc_2/ N\gamma_2$ for the upper energy window (266-369 keV). The ordinate of the upper graph is the APPC count rate, N_{APPC}, adjusted for the effect of the lower energy window by using the fitted parameters. The ordinate of the lower graph represents the absolute residuals.**

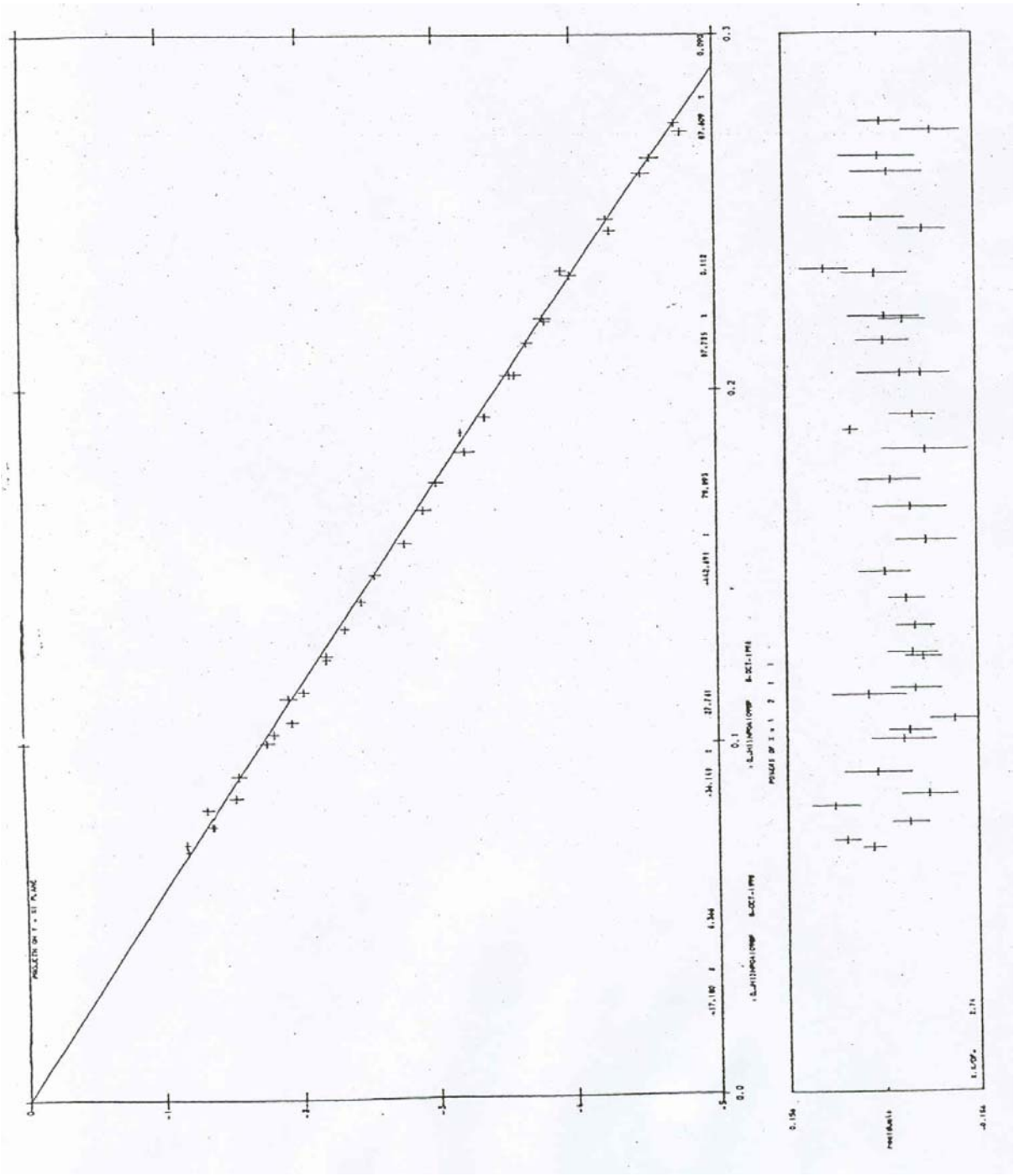


Figure 7: **$4\pi(\alpha\beta)$-γ method (NPL). Two-dimensional efficiency extrapolation, showing one aspect of the fit. Another aspect of the same fit is shown in figure 6. The abscissa is $(1-\varepsilon_1)$ where $\varepsilon_1 = Nc_1/ N\gamma_1$ for the lower energy window (approx 50-120 keV).The ordinate of the upper graph is the APPC count rate, N_{APPC}, adjusted for the effect of the upper energy window by using the fitted parameters. The ordinate of the lower graph represents the absolute residuals.**

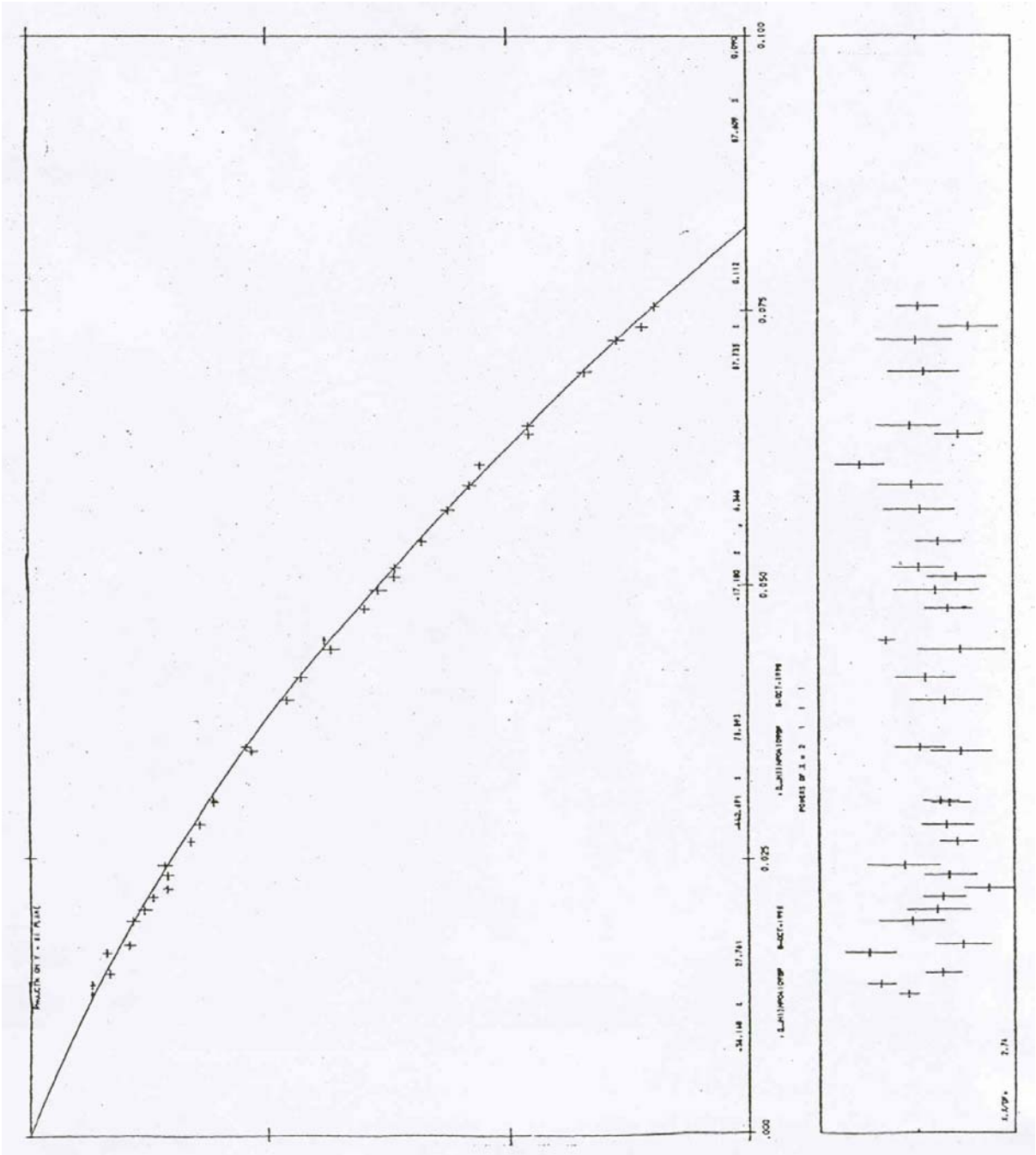


Figure 8: **$4\pi\alpha$ method (PTB).The ^{237}Np activity as a function of $(f_d)^{-0.5}$, where f_d is the dilution factor.**

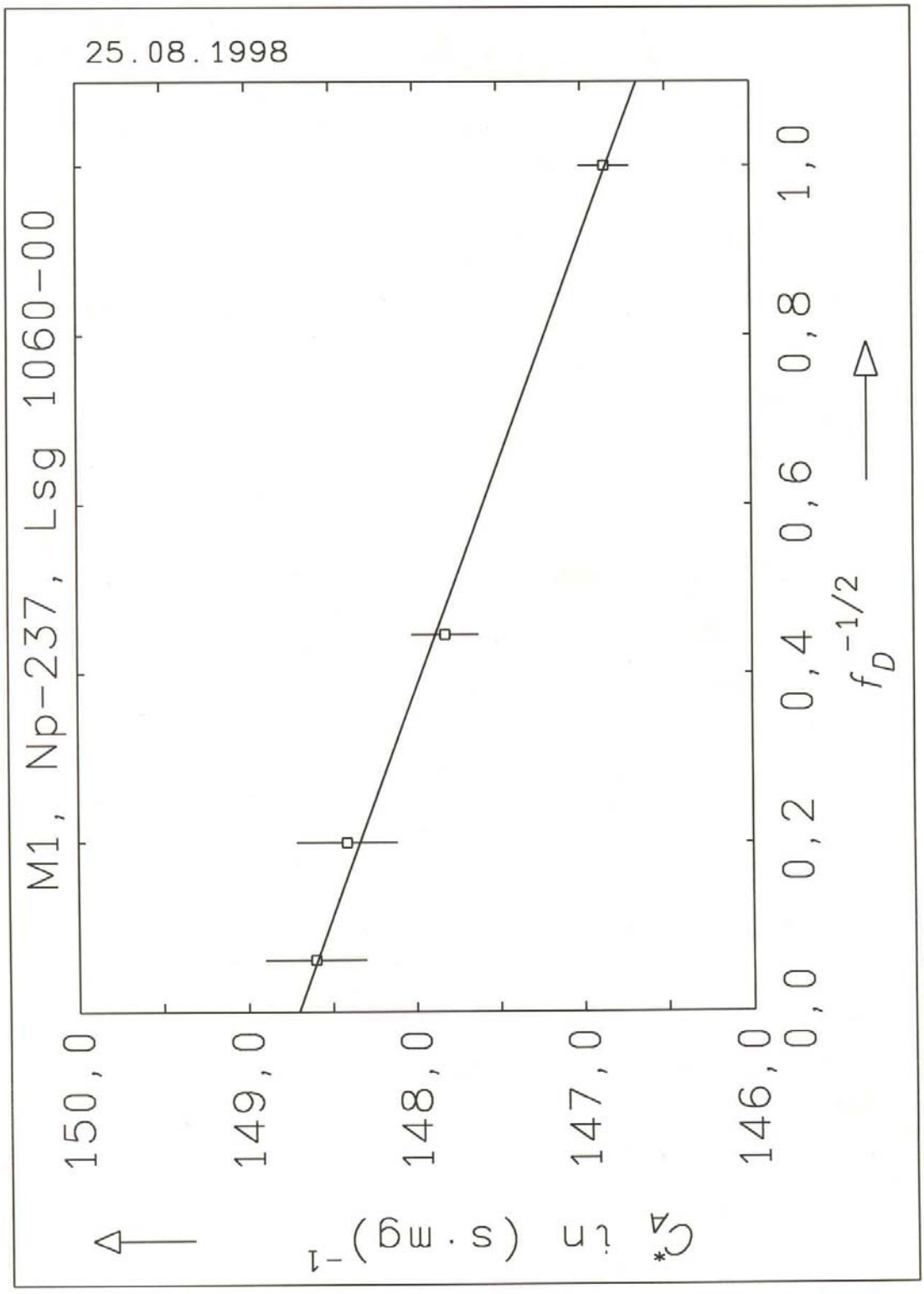


Figure 9: Secondary activity measurements. The efficiency calibration curve of a germanium detector (BIPM).

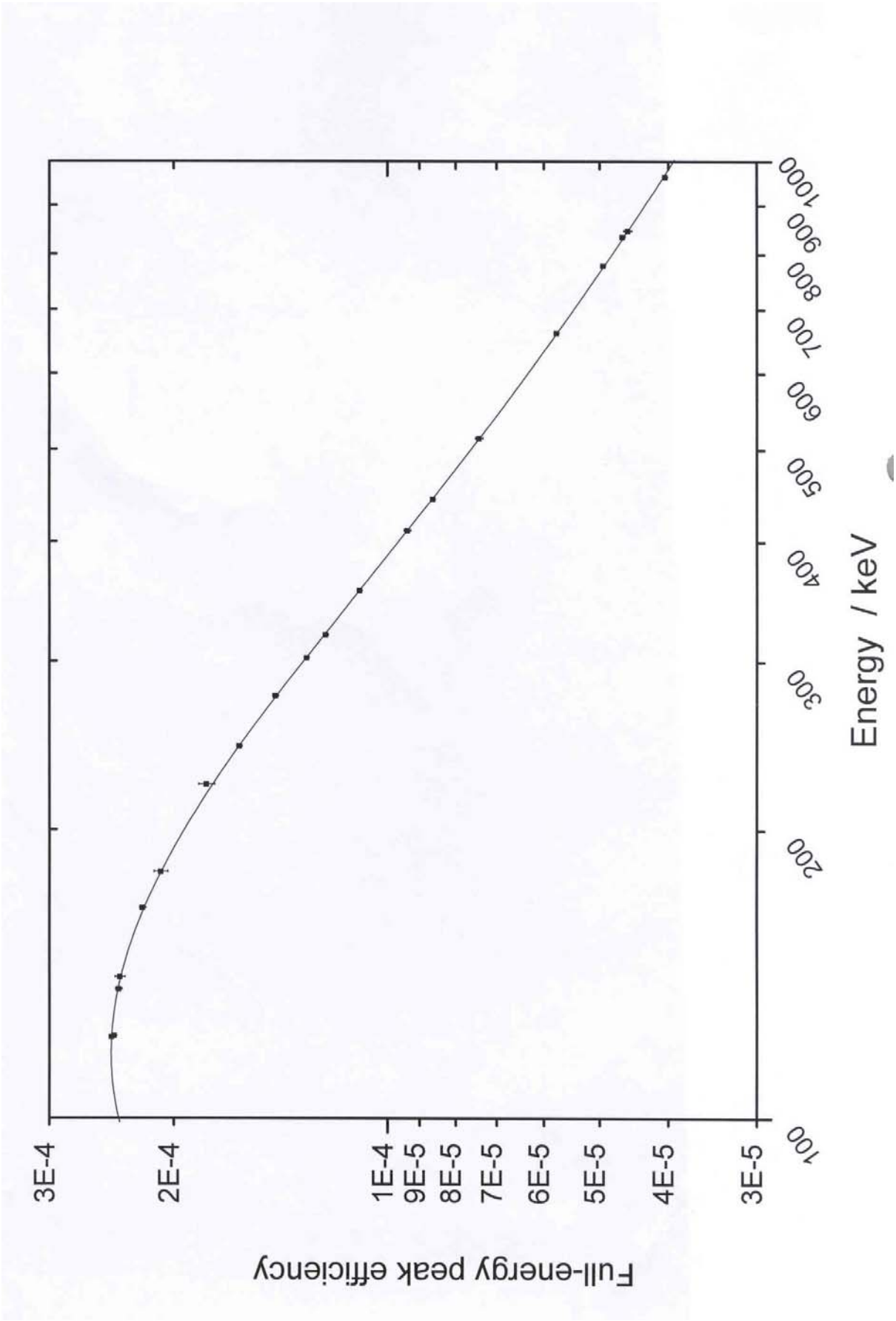


Figure 10: **^{237}Np activity concentration results, showing primary and secondary measurements and their respective weighted means. The uncertainty range represents ± the standard uncertainty.**

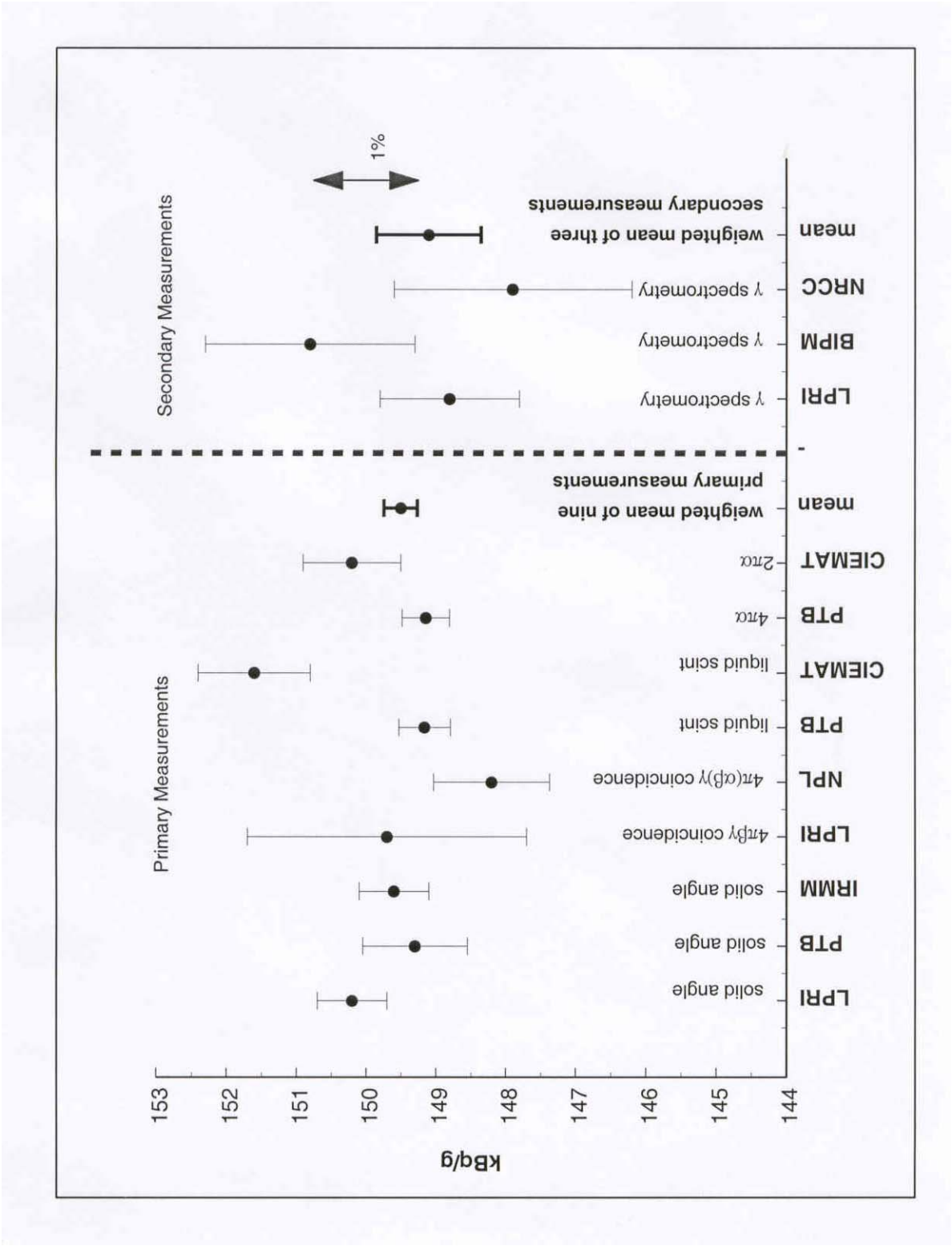


Figure 11: Determination of ^{237}Np absolute alpha emission probabilities (IRMM).The source and PIPS detector geometry, showing the bending magnet and diaphragm.

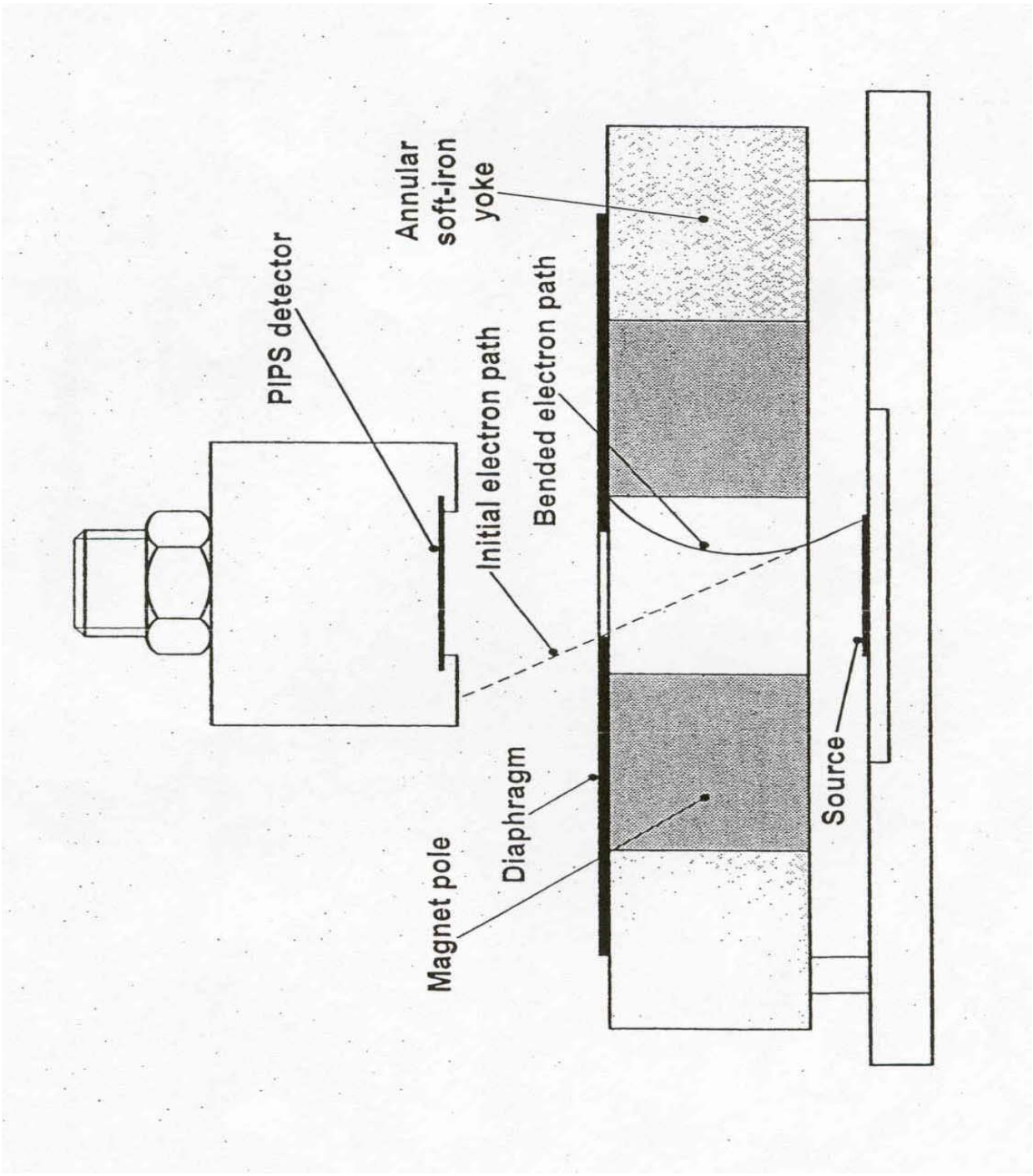
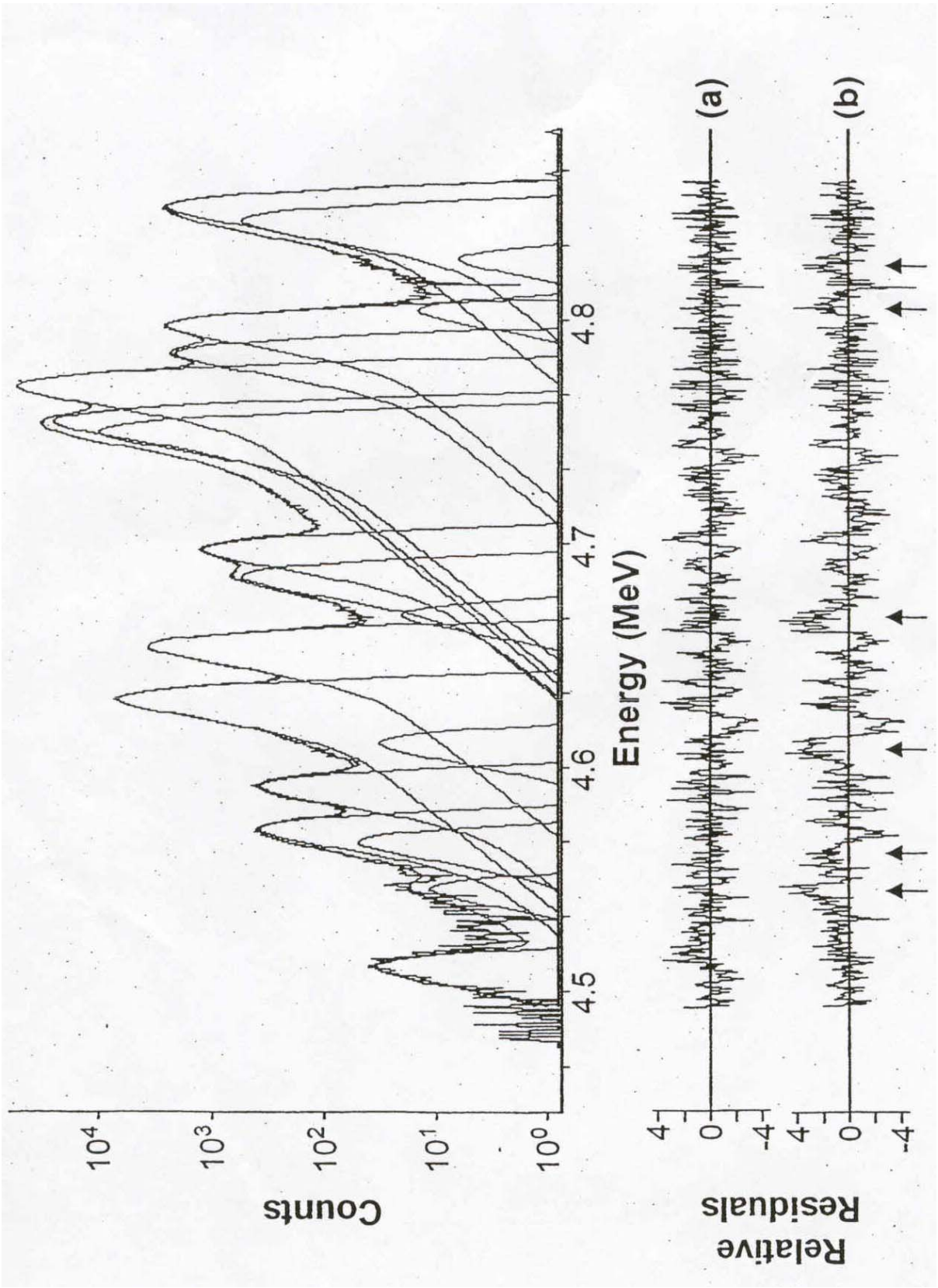


Figure 12: Determination of ^{237}Np absolute alpha emission probabilities (IRMM). Alpha particle spectrum illustrating the deconvolution of 20 lines with residuals (a). The residuals (b) relate to an initial fit to 14 lines, revealing a possible 6 further lines.



Appendix The definition of statistical terms

The equations used to evaluate mean values, uncertainties etc. are given below, defining the various terms. These definitions are the standard classical definitions. The term 'uncertainty' refers to the 'standard uncertainty', either of an individual result or of a mean result. A 'standard uncertainty' is the standard deviation of that result.

Suppose x_i is the i^{th} result of a total of n results, and the uncertainty of x_i is $u(x_i)$. For convenience, define $w_i = \frac{1}{[u(x_i)]^2}$. All the summations below are from i = 1 to n.

Weighted results:

mean = $\bar{x}_m = \frac{\sum w_i x_i}{\sum w_i}$

external uncertainty of the mean = $\sqrt{\frac{\sum w_i (x_i - \bar{x}_m)^2}{(n-1)\sum w_i}}$

% external uncertainty of the mean = $100 \left(\frac{\text{external uncertainty}}{\text{mean}} \right)$

degrees of freedom (df) = n-1

internal uncertainty of the mean = $\sqrt{\frac{1}{\sum w_i}}$

reduced $\chi^2 = \frac{\chi^2}{n-1} = \frac{\sum w_i (x_i - \bar{x}_m)^2}{n-1}$ and $\frac{\text{external uncertainty}}{\text{internal uncertainty}} = \sqrt{(\text{reduced } \chi^2)}$

Thus if (reduced χ^2) < 1, the external uncertainty is smaller than the internal uncertainty.

Unweighted results:

These can be derived from the above weighted case by setting all w_i to be the same.

mean = $\bar{x}_u = \frac{\sum x_i}{n}$

external uncertainty of the mean = $\sqrt{\frac{\sum (x_i - \bar{x}_u)^2}{(n-1)\, n}}$

% external uncertainty of the mean = $100 \left(\frac{\text{extenal uncertainty}}{\text{mean}} \right)$

degrees of freedom (df) = n-1

The concept of internal uncertainty and χ^2 are not relevant to the unweighted case.