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Development of Resin Bead Sampling and Analitical Technique Study of Resin Bead Measurement Technique for Uranium and Plutonim/Result of Joiut Experiment

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要　旨

再処理工場入量計量槽の保障措置として，現在，国およびＩＡＥＡによる試料の収去が行なわれているが，収去試料の輸送に当って，１バッチ当り，Ａ型輸送容器一つを必要とするのが現状である。このような輸送問題を軽減するため，極微量の試料（ウラン・プルトニウム各数mg）で分析可能なレジンビード法が来国オークリッジ国立研究所を中心に開発された。この技術はＴＡＳＴＥＸ時代に導入され，その後ＪＡＳＰＡＳの一つの開発項目として動燃事業団が主体となり，ＩＡＥＡとの共同研究を続けているものである。これまで７回の共同実験が実施され，技術的にもある水準に達したと思われるが，また同時にレジンビード技術の難点も明らかになった。

これらの共同実験では，動燃が試料の調整・輸送を担当し，ＩＡＥＡ側で分析するという形態をとっているが，これとは別に事業団としてレジンビード測定技術の検討も実施してきた。レジンビード技術は上記のように輸送上のメリットが最もクローズアップされているが，測定面においてもウラン・プルトニウムを分離することなく測定できるという利点もあり，施設側での分析法として開発・検討を進める必要があった。

本報では，レジンビード法によるウラン・プルトニウムの測定技術について検討結果を報告するとともに，第３回から第７回まで行なわれたＰＮＣ－ＩＡＥＡ間共同実験結果についても合わせて報告する。

再処理工場工務部分析課

Development of Resin Bead Sampling and Analytical Technique

---Study of Resin Bead Measurement Technique for Uranium and Plutonium / Result of Joint Experiment---

(Final Report of JASPAS JC-4)

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Development of Resin Bead Sampling and Analytical Technique

---Study of Resin Bead Measurement Technique for Uranium and Plutonium / Result of Joint Experiment---

(Final Report of JASPAS JC-4)

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ABSTRACT

So far, samples have been taken by both Japan Government and the International Atomic Energy Agency (IAEA) from the feed accounting tank of the Reprocessing Plant.

Upon transporting the samples, one A-type transport container per batch sample has been required. To simplify the transport of samples, the resin bead technique requiring the trace amounts of samples (several mg for uranium and for plutonium) has been developed with the Oak Ridge National Laboratory, USA being the center. This technique was introduced into the Power Reactor and Nuclear Fuel Development Corporation (PNC) as part of the TASTEX project, and then has been incorporated intothe JASPAS project as one of the joint researches between the PNC and the IAEA, in which the PNC has played a leading role. Up to now, joint experiments have been performed seven times, and the resin bead technique may have reached a certain technical level with a few technical problems.

In these joint experiments, the PNC prepared and transported samples, whereas the IAEA analysed them. In addition, the PNC has investigated the resin bead technique independently. As mentioned above, the most outstanding merit of the resin bead technique lies in the simplified transport of samples. The technique is also provided with another merit by which uranium and plutonium can be measured without separating them from each other, leading to the necessity of research and development of it on the part of the Reprocessing Plant.

This paper describes the results of investigation on the measurement technique of uranium and plutonium by means of the resin bead technique, together with the results from the 3rd to 7th PNC-IAEA joint experiments.

INTRODUCTION

The development of the resin bead sampling and analytical techniquestarted in 1979 as the Task-J of the TASTEX project under the cooperation between Japan and the US to verify the effectiveness of the method as a safeguards technique.

The resin bead technique was first invented in the Oak Ridge National Laboratory (ORNL), Tennessee, USA to adsorb uranium and plutonium contained in a feed-accounting sample (spent-fuel-dissolved solution) into ion exchange resin beads, which are in turn transported to the Safeguards Analysis Laboratory(SAL) for simultaneous analysis of uranium and plutonium without separation of them by using a mass spectrometer[1) 2)]. Since the main objective of this technique was to simplify the transport of the feed-accounting samples, emphasis was not placed on the measurement technique itself on the part of the Reprocessing Plant. However, with the progress in the atomization of mass spectrometers and the improvement in their performance, the resin bead technique has been investigated in many analytical laboratories worldwide. In comparison with the conven-tional sample solution application method, this technique enables the pretreatment step to be automated to some extent in addition to possible simultaneous measurement of uranium and plutonium without separating them from each other; accordingly, the Analysis Laboratory, Takai Reprocessing Plant, PNC (PNC/TRP) recognized the necessity of investigating this technique, and has investigated it since 1982. As a result, desirable data (e.g., an accuracy of 0.1% for U-235/U-238 (NBS U-500)) to be explained later were obtained.

In February, 1983, the PNC/TRP invited Mr.R.Fiedler, who is one of the specialists of the resin bead technique and is working for the IAEA, to introduce the IAEA's technique and to exchange views, while the PNC/TRP had investigated its own measurement technique.

To develop the technique relating to the preparation of resin beads, a glove box exclusively for resin bead sampling was installed, and a robot for the automation of pretreatment was investigated. Since the resin bead technique handles the trace amounts of uranium and plutonium, contamination at the time of sample preparation gives the greatest effect on the results of analysis. However, the installa-tion of the glove box exclusive for sample preparation and the introduction of the robot for automation of pretreatment could completely eliminate this undesirable effect.

Chapter 1 of this paper reports the results of the investigation performed by the PNC on measurement techniques, the technique introduced by Mr.R.Fiedler, IAEA's specialist, and the results of experiments obtained by using it. Chapter 1 also reports the development of techniques associated with sample preparation.

In addition to the development of resin bead analytical technique, the joint experiments as field tests have been carried out seven times to find out a suitable sample preparation method for uranium and plutonium contained in the feed accounting tank by using resin beads.

The first joint experiment[3] was performed by the PNC, the ORNL and the IAEA. In this experiment, the sampling method was not accurate, leading to the contamination of samples and unexpected level of operators' exposure at the time of sample preparation. Accordingly, the sample preparation method was discussed between the three parties to revise the operation manual completely.

On the basis of the outcome of the first joint experiment, the second one[4][5] was performed. In the second joint experiment, the samples prepared in accordance with the new operation manual were transported to the ORNL and the IAEA (SAL) for measurement. The results of measurement were compared with those by the conventional PNC/TRP technique, confirming that the former was far better than the latter.

In the third joint experiment, sample preparation after secondary sampling and spiking, which was the key factor for operators' exposure during sample preparation, was revised to be done in the analytical cell[6]. With the end of the TASTEX project, comprehensive evaluation was carried out for it, and the Task-J was decided to be further investigated between Japan and the IAEA as the JASPAS JC-4. Since the third joint experiment, the resin bead technique has been developed under the JASPAS project.

The fourth joint experiment was done to build up actual experiences before the glove box line exclusively for resin bead sampling was installed. The results of the experiment were not so good as those of the previous experiments.

In the fifth joint experiment, three glove boxes exclusively for resin bead sampling were installed and samples were prepared in them, leading to the complete elimination of the contamination problem.

In the sixth joint experiment, Japan's Safeguards Analysis Laboratory operated by the Nuclear Material Control Center (hereinafter referred to as the NMCC) joined the experiment for the first time, and the resin bead measurements were carried in the three parties, i.e., the PNC, the NMCC and the IAEA, in parallel.

In the seventh joint experiment, in addition to the glove boxes exclusively for resin bead pretreatment, a robot to atomize the pretreatment operation was introduced to prepare samples. The results demonstrated that resin bead samples could be automatically prepared by the robot.

Chapter 2 of this paper will report the results of the third to the seventh joint experiments in detail.

Chapter 1 Development of Analytical Uranium and Plutonium in Resin Beads

[1] Investigation of Resin Bead Analytical Technique in PNC

1. Introduction

So far, the resin bead technique has been developed to simplify the transport of samples taken for the purpose of safeguards; accordingly, the technique has been promoted from the start of its development to establish a sample preparation method for facilities to be inspected. However, the merit of the resin bead technique, i.e., possible simultaneous analysis of uranium and plutonium without separating them from each other, was considered to be beneficial for the routine analysis of the Reprocessing Plant, so the application of the resin bead technique to the analytical operations in the Plant has been investigated to simplify method of analysis.

The resin bead analytical technique was devisled in the ORNL, followed by experiments carried out in several countries with the IAEA (SAL) being the center. In 1982, under the auspices of the IAEA the joint analysis "TIGR 82" by means of the resin bead measurement was performed, and the results obtained by several countries were well coincided with each other. However, the resin bead analytical technique was not established worldwide at first, so the laboratories of each country participating in "TIGR 82", including the PNC/TRP, performed the experiment independently. The PNC/TRP followed the conventional method, and measurement by using a triple filament was attempted, whereas coating agents were tested by using a single filament with favorable results.

2. Experiments and Results

2-1. Confirmation of Amount of Samples Necessary for Coating Method

Initially, little information on measurement was available and it took relatively long time to purchase measuring (single) filaments, so the authors tried to conduct a series of experiments by using the conventional triple filaments. Because the resin bead is considered to adsorb nanogram-order (10^{-9} g) nuclear material, a side filament was coated with 1 to 20 ng nuclear material was coated for measurement. As a result, it was found that when the amount of sample was 3 ng or more, measurement could be done for sufficient time (about 50 min for an ion intensity of 1×10^{-13} A) with an accuracy of 0.33% (n=8).

2-2. Measurement of Resin Bead by Triple Filament

The central part of a both side filament was made boat-shaped, and a uranium (NBS-500) adsorbed resin was mounted in it for measurement. As a result, a coefficient of variation (CV%) of 0.42% was obtained.

2-3. Investigation of Measurement by Single Filament

Generally, the measurement of resin bead is carried out by using the single filament. Since the ionization temperature of plutonium is lower than that of uranium, plutonium is measured at first, followed by uranium. This is because upon the simultaneous measurement of uranium and plutonium, the difference in the ionization temperatures of each element is made use of. In this case, the single filament is desirable because of easy temperature control.

Consequently, several experiments were performed by using the single filament based on the results of the triple filament experiments described in the preceding subsection. As to the shapes of the filaments, the boat

type and the normal (flat) type were used. In the case of the boat type filament, are sin bead was mounted on the filament, and then caulked. The coating agents used were 1) graphite solution, 2) glycerin solution and 3) dilute nitric acid (0.01 M). The effect of these coating agents is considered to make ionization heat for the resin bead on the filament uniform and thereby to stabilize beams.

The results of the experiments revealed that the application of the coating agents except the glycerin solution could give stable accuracy. As to the normal-type filament, however, the probability of finishing measurement was as low as about 50% because of the resin bead dropping from the filament.

Table 1 shows the results of measuring resin beads which adsorbed the standard amounts of nuclides.

Table 1 Results of resin bead measurement in the PNC

	U-235/U-238	CV %	n	Pu-240/Pu-239	CV %	n
NBS010	0.010198	0.21	10			
NBS500	1.004964	0.14	10			
NBS947				0.240625	0.09	7
NBS500+NBS947	1.006730	0.11	5	0.241413	0.19	5

3. Conclusions

A series of resin bead measurements were carried out, and it was confirmed that desirable accuracy could be obtained internally and externally, but that the resin bead technique was accompanied by the following problems:

1) Since the amount of a sample is extremely small, the effect of mass fractional distillation was great, and so the result was sometimes lower than the theoretical value.
2) For uranium-plutonium mixed samples, the separation of m/e 238 was extremely difficult. When plutonium was measured, uranium was ionized to some extent and contributed to an error, resulting in an accuracy of about 40% for Pu-238/Pu-239 contained in the mixed sample.
3) Upon measurement, the resin bead must be fixed on the filament. The width of the filament is as small as 0.7 mm, so it requires a great deal of skill to fix the fine bead on the filament. Further, when the resin bead technique is adopted for routine analysis, errors due to cross-contamination etc. might tend to occur.

[2] Invitation of Mr.R.Fiedler, a Staff of the IAEA-SAL

The PNC/TRP had invited Mr.R.Fiedler, the mass spectrometer engineer of the IAEA-SAL, from Feb.13 to Feb.24, 1984 to introduce the program (software) for VG mass spectrometer developed by the IAEA into the VG system of the PNC. Initially, the application of the program was considered to be easy for the purpose of demonstrating the program, but differences in hardware (system monitor, magnet unit and interface unit) between the IAEA and PNC/TRP systems caused some difficulties. Eventually, the problems were solved, and debugging was completed within schedule. The report written by Mr.R.Fielder and his schedule are attached herewith.

ATTACHMENT 1

Visit to PNC-NMCC-JAERI
13 To 24 Feb. 1984

R. FIEDLER

SAL (Seibersdorf) has offered to adapt its software for VG-instrument which allows to measure resin beads containing U, Pu and a mixture of U+Pu for PNC, JAERI and NMCC.

In an introductional meeting the time schedule was fixed for the adaptation of the software for the 3 laboratories. The results of the TIGR-82 measurements done at PNC and a conclusion has been presented by PNC-staff. [Se Attachment 1] A first short introduction into the software layout was given. SAL's experience in handling resin beads has been described. The problems of resin bead measurements were discussed.

1) PNC

The adaptation of the software was started at PNC. The VG-mass spectrometer of PNC has 3 main differences compared to the SAL mass spectrometer.

a) System Monitor (PNC) System Analyser (SAL)
b) Magnet system
c) Interface differences

Many problems have arised when the software debugging has started. The layout of the SAL software is to use sub-programmes, which allow a very simple transfer of data and parameters. It could be figured out that the magnet can not be treated when a sub-program is used. Further on the behavior of the inferface is very different to that of SAL. Delays are needed more often as this is necessary at SAL when instructions are sent one after the other to the interface.

When all this was figured out and verified the whole data taking sequence of the existing software had to be rewritten. Only these sub-programmes which have been working could stay as they have been. The rest (mainly centering of the peak, data taking and the sequence for the individual measurement of U, Pu) had to be changed to subroutines, all these changes required more time than foreseen at the start of the work.

The final debugging of the software was very time cousuming and many problems showed up when measurements have been started.

The software for PNC is capable to measure resin beads containing U, Pu and a mixture of U and Pu. The loading procedure used at SAL was demonstrated. The resin bead is fixed using a sugar solution with rhenium powder. The rheniun powder should cover the resin bead.

The results received using the modifed software show very stable conditions (ion current) for U, Pu and the Pu measurement of a mixed bead and is not as stable on the U measurement following the burn off of Pu. A similar behavior has been observed at SAL. [See Attachment 2]

2) JAERI

An elder version of the software has been sent to JAERI last summer. In cooperation with Mr. Okazaki debugging work has been done and enabled JAERI to measure mixed resin beads.

While working at PNC a copy of the new software has been transfered to JAERI and adaptation has been carried out by Mr. Okazaki. At JAERI it was only neccessary to do minor changes on the software and it could be used for the measurements. The mass spectrometer of JAERI has a very similar lay out as compared to that of SAL. [See Attachment [See Attachment 3]

3) NMCC

Similar to JAERI and elder version of the software has been sent to NMCC. Mr. Tsutaki suggested a few changes as the instrument at NMCC has a diffent magnet system but a similar interface/as compared to SAL. A few statements in the magnet routines and the change of two instruction statements for the magnet and the digital integrator have been necessary to get the software working. [See Attachment 4]

4) Conclusion

The laboretories of PNC, JAERI and NMCC get a software package which allows to measure resin bead samples containing U, Pu and mixed U, Pu. On mixed beads a correction for the U-238 contamination on Pu-238 is possible, but can not be perfect. Therefore results obtained by α-spectrometry for Pu-238 seem to be the solution for this problem.

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[Attachment 1]

Outline of experiment at PNC. TRP-Lab

[1] Confirming Pu amount adsorbed on a resin bead (TIGR 82 sample)

1) Procedure: 1. take a resin bead (average size) and put it on a small tray
2. drop water (one drop) on the resin bead heat (bake) the tray and measure Pu content using α-counting

2) Results : 1. Pu amount on a resin bead adsorbed Pu only

Sample No.	Pu Amount (ng)
1	6.61
2	6.88
3	6.14
4	7.41
5	9.02

2. Pu amount on a resin bead adsorbed Pu and U

Sample No.	Pu Amount (ng)
1	4.02
2	4.38
3	4.84
4	6.84
5	4.28

[2] Mounting and measurement conditions

1) Preparation: 1. Prepare solution; 2.4mg U/10ml (8N HNO_3) (U: NBS 010, U 500)
2. take resin beads (~ 1000 beads; conditioned in HNO_3 - 8N) and soak them in above solution

3. Stir it by vibrating mixer for 20 minutes
4. Pour it to special column and leave it overnight (dryness)

2) Mounting:

Condition									
Filament type	Single Boat				Single flat type				
Dropped solution	Water containing carbon powder →			HNO_3 0.01N	Water containing carbon powder →				HNO_3 0.01N
Sample	U-500				U-010				
Experiment No	1	2	3	4	5	6	7	8	9

Preheat : Filament current; 1.2 A (5 min.)

run number : 10

3) Results: U-500

EXP No	1	2	3	4
Filament current	4.23 A	4.23 A	3.44 A	3.52 A
Aiming current	1×10^{-13} A	1×10^{-13} A	1×10^{-13} A	1×10^{-13} A
R 58	1.006286	1.006769	1.010879	1.004922
R 58 C.V.%	0.042	0.082	0.028	0.044
R 48	0.010652	0.010666	0.010728	0.010568
R 48 C.V.%	0.100	0.146	0.010728	0.162
R 68	0.001544	0.01606	0.001580	0.001540
R 68 C.V.%	0.304	0.356	0.624	0.291

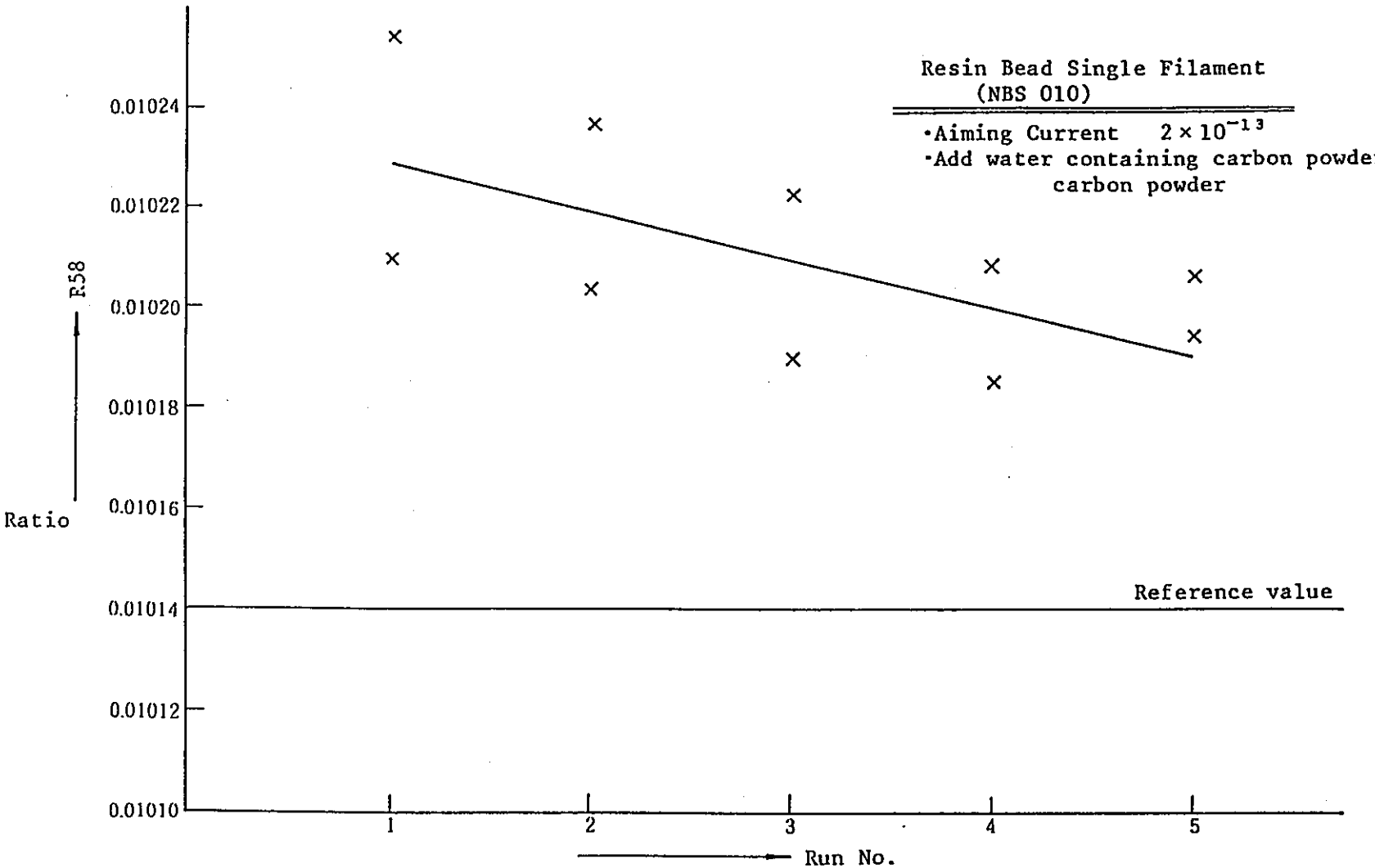
U-010

No.	5	6	7	8	9
Filament current	3.574 A	3.435 A	3.844 A	3.748 A	3.594 A
Aiming current	2×10^{-13} A	2×10^{-13} A	3×10^{-13} A	3×10^{-13} A	2×10^{-13} A
R 58	0.010255	0.010210	0.010100	0.010225	0.010185
R 58 C.V.%	0.073	0.091	0.079	0.075	0.094
R 48	0.000085	0.000061	0.000072	0.000069	0.000071
R 48 C.V.%	0.528	1.686	1.183	1.176	1.041
R 68	0.000080	0.000061	0.000071	0.000072	0.000069
R 68 C.V.%	1.032	1.461	0.523	0.979	1.409

- Obvious differences between neither the condition containing carbon and diluted HNO_3 nor two types of filaments were not observed.

4) Measurement value v.s. run number (time).

Results are shown in Fig. 1.



Each run consists of 10 scans.

Fig. 1

5) Repetitions on same condition.

(Precision among beads, U 010)

Bead No.	Filament current	R 58	R 58 C.V.%	R 48	R 48 C.V.%	R 68	R 68 C.V.%
1	3.628A	0.010203	0.096	0.000071	0.952	0.000070	1.574
2	3.608A	0.010224	0.081	0.000070	0.573	0.000069	1.042
3	3.750A	0.010207	0.055	0.000072	2.067	0.000070	1.716
4	3.699A	0.010205	0.053	0.000066	2.745	0.000063	4.422
5	3.713A	0.010216	0.050	0.000079	3.269	0.000076	2.305
6	3.716A	0.010216	0.090	0.000075	1.034	0.000072	1.448
$\bar{X}$		0.010212		0.000072		0.000070	
C.V.%		0.079		6.16		6.06	

Measurement repetitions on each bead; 15

Aiming current; 2×10^{-13} A

[3] Experiment on measurement of mixed (Pu, U) Sample

1) Procedure; See "Measurement procedure of resin bead sample at PNC-RP-Lab"

2) Results

Experimental results of measuring mixed sample is shown in Table 4.5 of "Resine bead measurement condition TIGR 82"

3) Interference of U-238 on measuring Pu isotopic ratios.

i) Correction of U-238 monitoring U-235 (NBS U-500)

(R 89) corr = (R89) meas - (R 59) meas (R 85) STD

(R 89) corr : corrected ratio $\frac{\text{Pu-238}}{\text{Pu-239}}$

(R 89) meas : measured ratio $\frac{\text{(Pu+U) - 238}}{\text{Pu - 239}}$

(R 59) meas : measured ratio $\frac{\text{U - 235}}{\text{Pu - 239}}$

(R 85) STD : known standard ratio $\frac{\text{U - 238}}{\text{U - 235}}$

Result of this correction is as follows;

	(R 89) meas	(R 59) meas	(R 89) corr	(R 85) STD
11	0.159796	0.157654	0.002095	1.0003
22	0.211290	0.205361	0.005867	
33	0.378557	0.376087	0.002357	
44	0.206479	0.204076	0.002342	
55	0.375042	0.367709	0.007223	
$\bar{x}$			0.003977	
σ			0.002395	
C.V. %			60.2 %	

[reference value; R 89 = 0.003565 (1983.7.1)]

[It seems to be difficult to correct interference of U in total measured peak consisting of miner peak (238) of Pu and major peak of U.]

ii) Correction of U-238 by α-spectometry measurement result of this correction is as follows;

	R 89 (corr)
1	0.003618
2	0.003621
3	0.003616
4	0.003717
5	0.003624
X	0.003619
σ	0.0000033
C.V. %	0.09 %

[reference value; R 89 = 0.003565 (1983.7.1)]

[It can be said that correction of (R 89)-Pu is possible by using α-Spectrometry.]

4) Interference of Pu-238 on measuring U isotopic ratios considering the prompt analysis of mixed (U and Pu) sample.

Measurement sequences are decided as follows;

	Seq.1	Seq.2	Seq.3	Seq.4	Seq.5	Seq.6
Aiming current	3×10^{-14}	1×10^{-13}	2×10^{-13}	1×10^{-13}	2×10^{-12}	2×10^{-13}

Pu measurement U measurement

After measurement of Pu, the ratio of U-238 and Pu-239 was monitored. When the ratio of $\frac{\text{Pu-239}}{\text{U-238}}$ is less than 1/5 in Seq. 4 ~ 5, the remained part of Seq.4 and Seq.5 is skipped and isotopic ratios of uranium are obtained in Seq.6. The result is shown in Table 4 of "Resin bead measurement condition TIGR 82" (The precision of R 58 (NBS010) is about 0.1%)

Recommended measurement

- U-238 on measuring Pu should be corrected by α-spectrometry.
- Current value should be raised [e.g. $2\times10^{-13} \rightarrow 2\times10^{-12}$] for complete ionization of Pu after Pu measurement for the sake of prompt analysis.
- It seems to be better way to monitor Pu-239 and to correct the slight interference of Pu during U measurement. (Seq. 6)

Problems

- correction of mass discrimination (especially U)
- homogeneity of resin beads and content of Pu or U in a resin bead
- Method of mounting

Resin Bead measurement condition (TIGR 82)

1. Mass spectrometry

VG ; ISSOMASS 54E

2. Acceelerting voltage

; 8 kV

3. Detector system

Daly	Resistance	1 × 10E11 (Ω)
	Supplied H. V.	16.7 (kV)
	Photomultiplier H. V.	820 (V)

4. Slit width

Source slit	Ws = 0.3 (mm)
Collector slit	wc = 1.0 (mm)

5. Measurement scheme

Sample Type	Measurment Ratio	Detector System	Aiming Current (A)	Number of scan
U1	1) R 48, R 58, R 68	D*1	1 10E-13	3
	2) R 48, R 58, R 68	D	2 10E-13	15
(NBS010)	3) R 45, R 65	D	1 10E-14	10
U2	1) R 48, R 58, R 68	D	1 10E-13	3
	2) R 48, R 58, R 68	D	2 10E-13	15
(NBS500)	3) R 58	D	2 10E-13	10
P1	1) R 89, R 09, R 19, R 29	D	1 10E-13	3
	2) R 89, R 09, R 19, R 29	D	2 10E-13	15
(NBS947)	3) R 58, R 89, R 09, R 19, R 29	D	2 10E-13	10
M1	1) R 09, R 19, R 29	D	3 10E-14	3
	2) R 89, R 09, R 19, R 29	D	1 10E-13	5
(NBS500+ NBS947)	3) R 58, R 59, R 89, R 09, R 19, R 29	D	2 10E-13	15
	4) R 58, R 59, R 89	F*2	1 10E-12	10
	5) R 58, R 59, R 89	F	2 10E-12	10
	6) R 48, R 58, R 68, R 89	D	2 10E-13	15

*1 Daly Detector

*2 Faraday cup Detector

6. Filament

Single (flat) filament
(cutting side parts of Ta-Re-Ta)

7. Mounting

1) take a resin bead with special needle and mount it on center of single filament.
2) drop HNO_3-8N (1 ~ 2 μℓ) on a bead and dry it.
3) drop HNO_3-0.01N (1 ~ μℓ) and dry it.

8. Measurement

1) Preheat
raise filament current to 1.2 A and hold the situation for 5 minutes.
2) Measurement
i) U1, U2
(1) raise filament current to 3.2 A in 5 minutes and subsequently do it with rate of 0.6A/min.
(2) measure U after total aiming current of 2×10^{-13}A is obtained. (Filament current: approximately 3.6 A)

ii) P1, M1
(1) raise filament current to 2.5 A in 5 minutes and subsequently do it with rate of 0.5 A/min.
(2) P1: measure Pu after total aiming current of 2×10^{-13} A is obtained. (Filament current: approximately 2.7 A)
M1: measure Pu and U after total aiming current of 2×10^{-13} A is obtained respectively.

[Refer "5.measurement scheme", Filament current;
Pu; approximately - 3.5 A
U ; approximately - 3.7 ~ 3.8 A]

Reproducibility of Replicate Resin Bead Analyses (U-NBS 010)

(No Correction for Fractionation Effectes) Date of Measurement

83 06 15 ~83 06 20

Table 1

Analysis	R 45		R 58		R 65	
	$\bar{X}$	C.V.%	$\bar{X}$	C.V.%	$\bar{X}$	C.V.%
1	0.005246	0.36	0.010173	0.08	0.007315	0.60
2	0.005444	0.41	0.010150	0.10	0.007296	0.58
3	0.005450	0.64	0.010179	0.05	0.007199	0.62
4	0.005357	0.35	0.010220	0.05	0.007057	0.73
5	0.005278	0.43	0.010213	0.07	0.006835	1.14
6	0.005477	0.73	0.010224	0.08	0.006962	0.43
7	———		0.010202	0.05	———	
8	0.005374	0.68	0.010204	0.09	0.006980	0.87
9	0.005388	0.89	0.010168	0.12	0.007024	0.65
10	0.005452	0.72	0.010248	0.08	0.007143	0.64
Mean	0.005385		0.010198		0.007090	
External Std dev.	0.000081		0.000022		0.000138	
External C.V.%	1.50		0.21		1.94	
Ref. Value.	0.005390		0.010140		0.006785	

Reproducibility of Replicate Resin Bead Analyses (U-NBS 500)

(No Correction for Fractionation Effectes) Date of Measurement

83 06 15 ~ 83 06 20

Table 2

Analysis	R 48		R 58		R 68	
	$\bar{X}$	C.V.%	$\bar{X}$	C.V.%	$\bar{X}$	C.V.%
1	0.010478	0.08	1.002842	0.03	0.001567	0.28
2	0.010456	0.09	1.003580	0.01	0.001546	0.35
3	0.010557	0.18	1.004390	0.06	0.001571	0.50
4	0.010533	0.16	1.006047	0.03	0.001551	0.33
5	0.010513	0.09	1.005965	0.02	0.001561	0.52
6	0.010509	0.11	1.005459	0.04	0.001556	0.22
7	0.010487	0.17	1.005177	0.04	0.001537	0.19
8	0.010480	0.11	1.003129	0.02	0.001548	0.32
9	0.010652	0.10	1.006286	0.04	0.001544	0.30
10	0.010666	0.15	1.006796	0.08	0.001606	0.36
Mean	0.010533		1.004964		0.001559	
External Std.dev.	0.000072		0.001398		0.000020	
External C.V.%	0.69		0.14		1.26	
Ref. Value.	0.010422		0.999698		0.001519	

Reproducibility of Replicate Resin Bead Analyses (Pu-NBS 947)

(No Correction for Fractionation Effectes) Date of Measurement

83.06.22 ~ 83.06.24

Table 3

Analysis	R 89		R 09		R 19		R 29	
	$\bar{X}$	C.V.%	$\bar{X}$	C.V.%	$\bar{X}$	C.V.%	$\bar{X}$	C.V.%
1	0.003637	0.20	0.240243	0.02	0.034211	0.05	0.015468	0.06
2	0.003615	0.23	0.240539	0.01	0.034649	0.08	0.015471	0.06
3	0.003605	0.20	0.240853	0.01	0.034345	0.04	0.015491	0.08
4	0.003589	0.12	0.240650	0.01	0.034355	0.04	0.015482	0.09
5	0.003617	0.15	0.240522	0.02	0.034974	0.02	0.015481	0.06
6	0.003635	0.11	0.240698	0.03	0.034027	0.04	0.015524	0.06
7	0.003629	0.16	0.240868	0.01	0.034335	0.04	0.015479	0.07
Mean	0.003618		0.240625		0.034414		0.015485	
External std.dev.	0.000017		0.000216		0.000309		0.000019	
External C.V.%	0.48		0.09		0.90		0.12	
*1 Ref. Value.	0.003565		0.241380		0.034024		0.015594	

*1 - 1983. 7. 1

Reproducibility of Replicate Resin Bead Analyses (NBS 947 + NBS 500)

(No Correction for Fractionation Effectes) Date of Measurement

83.06.27 ~ 83.06.30

Table 4

(NBS 500)

Analysis	R 48		R 58		R 68	
	$\bar{X}$	C.V.%	$\bar{X}$	C.V.%	$\bar{X}$	C.V.%
1	0.010531	0.06	1.007794	0.01	0.001536	0.27
2	0.010535	0.12	1.006459	0.02	0.001528	0.49
3	0.010515	0.11	1.006057	0.04	0.001546	0.41
4	0.010560	0.15	1.007940	0.01	0.001536	0.31
5	0.010494	0.25	1.005400	0.11	0.001505	0.75
Mean	0.010527		1.006730		0.001530	
External std.dev.	0.000025		0.001106		0.000015	
External C.V.%	0.23		0.11		1.01	
Ref. Value.	0.010422		0.999698		0.001519	

Reproducibility of Replicate Resin Bead Analyses (NBS 947 + NBS 500)

(No Correction for Fractionation Effectes Date of Measurement 83.06.27 ~ 83.06.30

Table 5

(NBS 947)

Analysis	R 89		R 09		R 19		R 29	
	$\bar{X}$	C.V.%	$\bar{X}$	C.V.%	$\bar{X}$	C.V.%	$\bar{X}$	C.V.%
1	0.159796	0.54	0.241255	0.03	0.034178	0.08	0.025600	0.07
2	0.211290	4.10	0.241667	0.07	0.034113	0.29	0.015522	0.45
3	0.378557	0.54	0.240990	0.01	0.033944	0.06	0.015400	0.14
4	0.206479	0.33	0.241077	0.03	0.033971	0.06	0.015501	0.07
5	0.375042	0.78	0.242078	0.03	0.034303	0.05	0.015682	0.08
Mean	0.266233		0.241413		0.034108		0.015541	
External std.dev.			0.000454		0.000149		0.000106	
External C.V.%			0.19		0.44		0.68	
*1 Ref. Value.	0.003565		0.241380		0.034024		0.015594	

*1 - 1983. 7. 1

Measurement procedure of resin bead sample at PNC-RP-Lab.

1. Instrument: VG ISOMASS 54E

2. Procedure of sample loading:
   1) take a resin bead containing sample (Pu, U) with special needle and load it on center of single Re filament*
   2) drop diluted nitric acid (0.01N)** 1 ~ 2μl on loaded bead
   3) dry filament by switching on current (raising current rate: 0.1 A/min. max. 0.5 A)

   * use flat single filament instead of boat type

   ** Notable results could not be obtained though other material (carbon, glycerine etc.) had been tasted.

3. Measurement procedure:
   1) Preheat

      raise filament current to 1.2 A and hold it in this situation for 5 minutes
   2) Measure (U, Pu mixture)

      used program: GPJ (general peak jumping)

      (1) raise filament current up to 2.2 A in 15 min. and subsequently do it with rate of 0.15 A/min

      (2) measure plutonium isotopic ratio 15 times over in Seq. 3 after total (239, 240, 241, 242, 238, 239) aiming current of 2×10^{-13} A is obtained; See next page (Seq. 1, and Seq. 2 is used for conditioning of Pu measurement.)
      Filament current: approximately 3.5 A
      (It takes 70 min. to complete Pu measurement.)

      (3) Raise filament current (total aiming current: 1×10^{-12} A) in Seq. 4, 5 and hold this sutuation monitoring 235, 238, 239

      (4) Skip remained program in Seq. 4 or 5 if ratio of 235/239 is attained to more than 5

      (5) Measure uranium isotopic ratio 15 times over in Seq. 6 after total aiming current of 2×10^{-13} A is obtained
      (Filament current: 3.7 ~ 3.8 A
      It takes less than 2 hours to complete all measurement.)

Procedure name: U + Pu GPJ (NBS 500 + NBS 947) Type: General Peak Jumping

	---- CENTER ----			----- SIDE -----			-- MARMUP TIMES (mins) --		
Filament	P-heat	Init	Max	P-heat	Init	Max	Preheat	Hold	Measure
Currents	1.20	2.00	5.30	0.00	0.00	0.00	05.0	05.0	05.0

Initial	eV	Z-bias	Z-focus	Slit	D-focus	D-bias	Extract	Source
values	510	560	430	600	800	550	350	710

Rhenum aiming current 0.0E + 00 Beam growth limit -1.5 to +1.5 % in 10 sec.

Sequence	1	2	3	4	5	6
Detector (F/D)	D	D	D	F	F	D
Aiming current	3.0E-14	1.0E-13	2.0E-13	1.0E-12	2.0E-12	2.0E-13
No. of runs	01	01	01	01	01	01
No. of cycles	03	05	15	10	10	15
Sequence type	07	04	04	09	09	06

Daly bias +0.000E+00 Faraday bias +0.000E+00

Start Grand Totals at Seq. No. 1

Procedures stored on file

Mix Spike (Resin Bead)	GPJ
Pu GPJ (NBS 947 only)	GPJ
U GPJ (NBS U 500)	GPJ
U GPJ (NBS U 010)	GPJ
Pu Spike	Putl
Pult 83-1	Putl
Uran Seido Kento-2	Urtl
Uran SEIDO KENTO	Urtl
Uran 83-1	Urtl
Uran Spike	Urtl
U500 Double Collector	UrtD

Peak jumping TYPE Number 1

Ratio 1 234/238
Ratio 2 235/238
Ratio 3 236/238

Intrf 1 234/234.5 = .500000

Channel	Mass	Integration time
z	233.540	
1	238.051	5
2	234.541	5
3	234.041	3
4	234.541	5
5	236.046	5
6	235.044	5

Peak jumping TYPE Number 2

Ratio 1 234/235
Ratio 2 236/235

Intrf 1 234/234.5 = .500000

Channel	Mass	Integration time
z	233.540	
1	235.044	5
2	234.541	5
3	234.541	3
4	234.041	5
5	236.046	5

Peak jumping TYPE Number 3

Ratio 1 234/238
Ratio 2 235/238
Ratio 3 236/238
Ratio 4 239/238

Intrf 1 234/234.5 = .500000
Intrf 2 236/236.5 = .500000

Channel	Mass	Integration time
z	233.540	5
1	238.051	5
2	234.541	3
3	234.541	5
4	234.041	5
5	236.046	5
6	235.044	5
7	236.546	5
8	239.052	5
9	236.546	5

Peak jumping TYPE Number 4

Ratio 1 238/239
Ratio 2 240/239
Ratio 3 241/239
Ratio 4 242/239

Intrf 1 238/238.5 = .500000
Intrf 2 240/240.5 = .500000
Intrf 3 241/241.5 = .500000

Channel	Mass	Integration time
z	242.559	5
1	239.052	5
2	240.544	5
3	240.054	5
4	240.544	5
5	241.057	5
6	241.557	5
7	242.059	5
8	238.551	5
9	238.051	5

Peak jumping TYPE Number 5

Ratio 1 238/239
Ratio 2 240/239
Ratio 3 241/239
Ratio 4 242/239
Ratio 5 235/239

Intrf 1 238/238.5 = .500000
Intrf 2 240/240.5 = .500000
Intrf 3 241/241.5 = .500000
Intrf 4 235/235.5 = .500000

Channel	Mass	Integration time
z	242.559	5
1	239.052	5
2	240.554	5
3	240.054	5
4	241.057	5
5	241.557	5
6	242.059	5
7	238.551	5
8	238.051	5
9	235.544	5
10	235.044	5

Peak jumping TYPE Number 6

Ratio 1 234/238
Ratio 2 235/238
Ratio 3 236/238
Ratio 4 238/239

Intrf 1 234/233.5 = .500000

Channel	Mass	Integration time
z	233.500	5
1	238.051	5
2	233.544	3
3	233.544	5
4	235.044	5
5	233.544	5
6	234.041	5
7	236.046	5
8	239.052	5

Peak jumping TYPE Number 7

Ratio 1 240/239
Ratio 2 241/239
Ratio 3 242/239

Channel	Mass	Integration time
z	233.500	5
1	239.052	5
2	240.054	5
3	241.057	5
4	242.059	5

Peak jumping TYPE Number 8

Ratio 1 235/238
Ratio 2 235/239
Ratio 3 238/239
Ratio 4 240/239
Ratio 5 241/239
Ratio 6 242/239

Intrf 1 235/235.5 = .500000

Channel	Mass	Integration time
z	233.500	5
1	239.052	5
2	240.054	5
3	241.057	5
4	242.059	5
5	235.544	5
6	238.050	5
7	235.544	5
8	235.044	5

Peak jumping TYPE Number 9

Ratio 1
Ratio 2
Ratio 3

Channel	Mass	Integration time
z	233.500	
1	239.052	5
2	238.050	5
3	235.044	5

Measurement procedure of resin bead sample at PNC-RP-Lab.

1. Instrument: MAT261

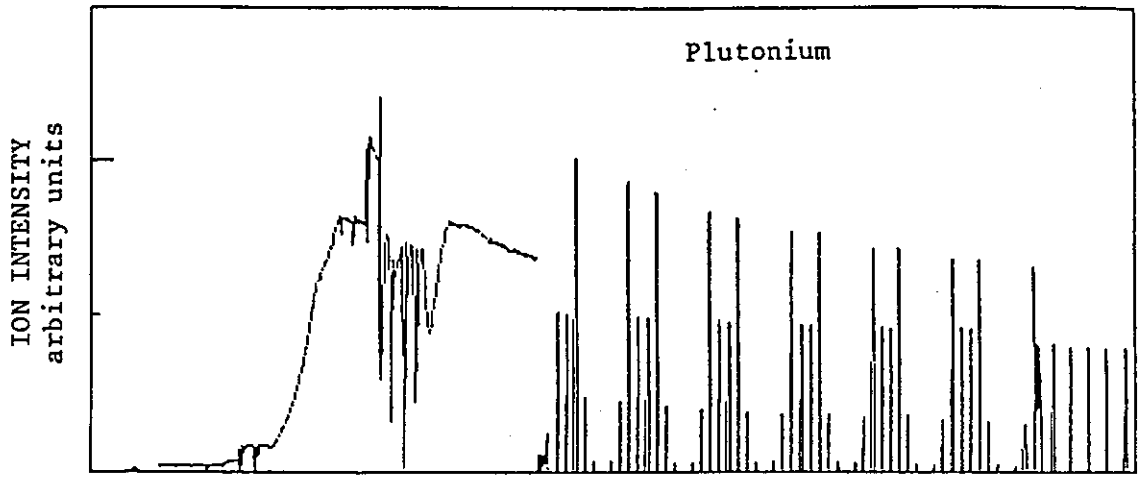
2. Procedure of sample loading:
   1) take a resin bead containing sample (Pu, U) with special needle and load it on center of single Re filament
   2) prepare mixtrue solution of Re powder with starch solution (10%) and drop it (only a drop) on loaded bead
   3) dry above filament with infrared-ray lamp for 15 minutes

3. Measurement procedure:
   1) Preheat
      raise filament current to 2.5 A gradually (in 15 minutes) and hold it at 2.5 A for 1 minute
   2) Measure (U, Pu mixture)
      (used program: MAT261 VERSION 2.0e)
      (1) raise filament current up to 2.8 A in 8 minutes and subsequently do it with rate of 0.2 A/min.
      (2) raise filament current with above ratio of until ion intensity 3×10^{-13} A (0.3 V) is attained
      (Filament current: approximately 3.9 A, 2300 °C
      It takes about 80 min. to complete Pu measurement)
      (3) raise filament current still more to find out uranium -238 ion after finishing Pu measurement
      (4) measure uranium isotopic ratio after uranium-238 intersity of 4×10^{-13} A (4V)
      monitor plutonium-239 during uranium measurement
      (It takes 3 hours to complete all measurement.)

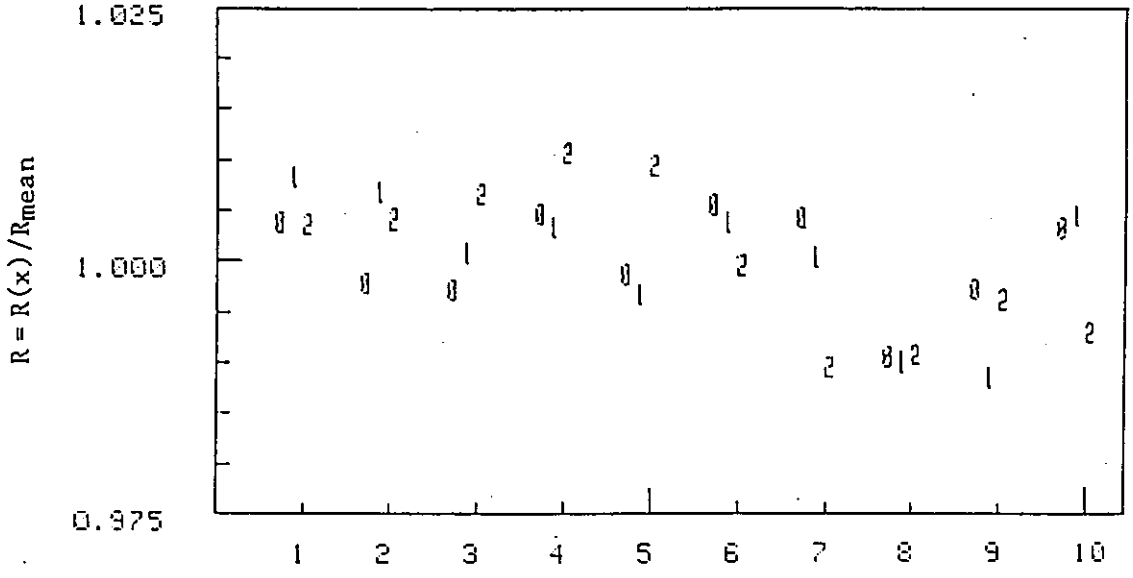
Test measurement with resin bead [Attachment 2]

PNC Mass spec measurements Log # 16

Resin bead 947/500 Pos #: 16



4



Resin bead Plutonium 947/500 Log #: 16

PNC MASS SPECTROMETRIC ANALYSIS Instrument: VG-54E

Operator: R Resin bead Date: 84022

Pos #	Log #	PNC id.	Type Code	Spike information	
16	16	947/500	4.1	0	0

N	238/239*	240/239*	241/239*	242/239	244/239*
1	.51520	.23725	.03247	.01522	.00001
2	.53679	.23583	.03243	.01523	.00001
3	.55802	.23570	.03223	.01526	.00001
4	.57880	.23744	.03231	.01533	.00001
5	.59599	.23605	.03210	.01531	.00001
6	.60673	.23765	.03233	.01516	.00001
7	.62417	.23737	.03222	.01501	.00000
8	.63986	.23413	.08188	.01502	.00000
9	.65264	.23571	.03183	.01510	.00000
10	.66760	.23709	.03235	.01506	.00001
Mean	.597579	.236422	.032215	.015169	.000007
Std	.050457	.001123	.000217	.000117	.000003
Rstd	8.443649	.474876	.672126	.770435	41.168825

*) The printout does not represent the actual data taking

	238	239	240	241	242	244
Atom%	31.76262	53.15215	12.56632	1.71229	.80627	.00035
Std	2.01871	1.42587	.34112	.04731	.02249	.00014
Weight%	31.64714	53.18196	12.62606	1.72762	.81687	.00036

Atomic weight: 238.9181

Mixed bead, U-238 interference on Pu-238, final values on Uranium printout

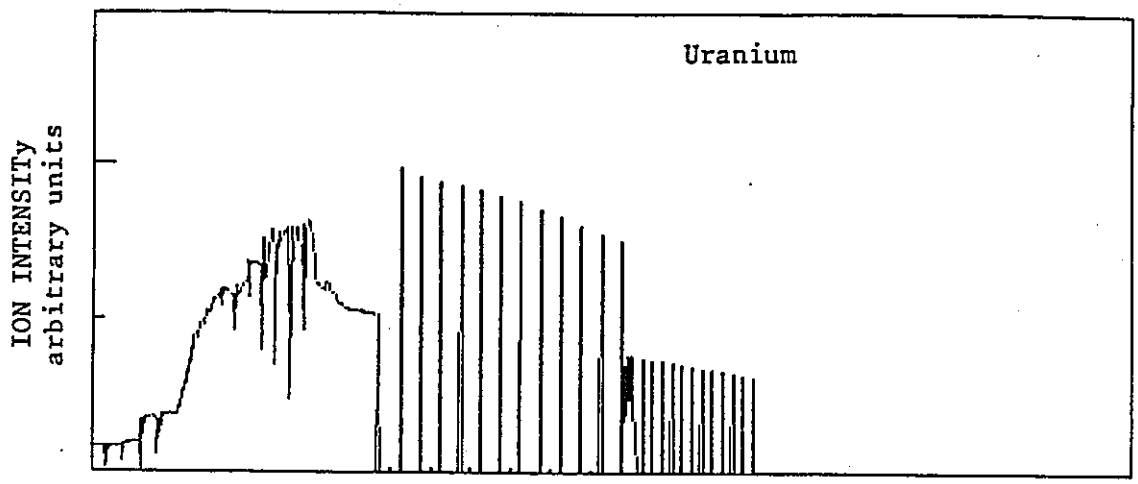
Filament current (A): 3.850

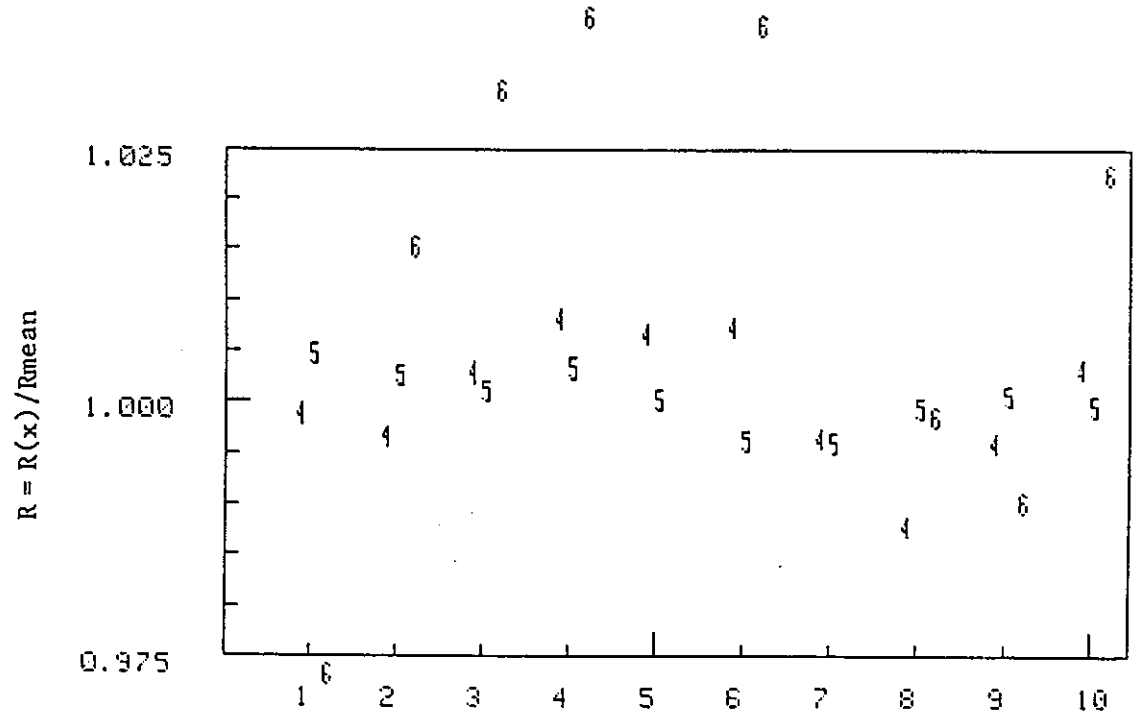
Average ion current of Plutonium: 11.1 E-14 amps

Total time spent on sample 48 mins 53 secs

PNC Mass spec measurements Log # 16

Resin bead 947/500 Pos #: 16





Resin bead Uranium 947/500 Log #: 16

PNC MASS SPECTROMETRIC ANALYSIS Instrument: VG-54E

Operator: R Resin bead Date: 84022

Pos #	Log #	PNC id.	Type Code	Spike information
16	16	947/500	4.1	0 0

N	233/238	234/235*	235/238	236/235*
1	0.00000	.01044	1.00409	.00145
2	0.00000	.01042	1.00213	.00152
3	0.00000	.01049	1.00057	.00154
4	0.00000	.01054	1.00279	.00155
5	0.00000	.01052	.99962	.00144
6	0.00000	.01053	.99560	.00155
7	0.00000	.01042	.99532	.00139
8	0.00000	.01033	.99882	.00149
9	0.00000	.01041	1.00007	.00148
10	0.00000	.01049	.99894	.00153
Mean	0.000000	.010459	.999797	.001494
Std	0.000000	.000067	.002846	.000053
Rstd	0.000000	.644531	.284620	3.526806

*) The printout does not represent the actual data taking

	233	234	235	236	238
Atom%	0.00000	.51981	49.69790	.07427	49.70802
Std	0.00000	.00372	.10005	.00263	.07035
Weight%	0.00000	.51433	49.38480	.07411	50.02675

Atomic weight: 236.5341

Burn off time for Pu: 3 min & 51 secs

Recalculated isotopic of Plutonium

	238	239	240	241	242	244
Atom%	-.65709	78.40483	18.53661	2.52580	1.18933	.00051

Filament current (A): 4.033

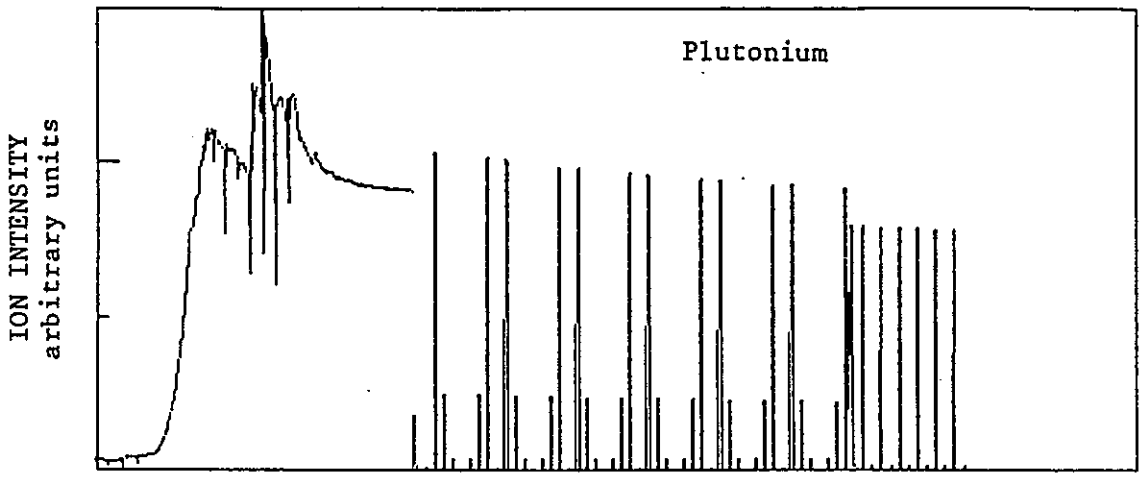
Average ion current of Uranium: 29.3 E-14 amps

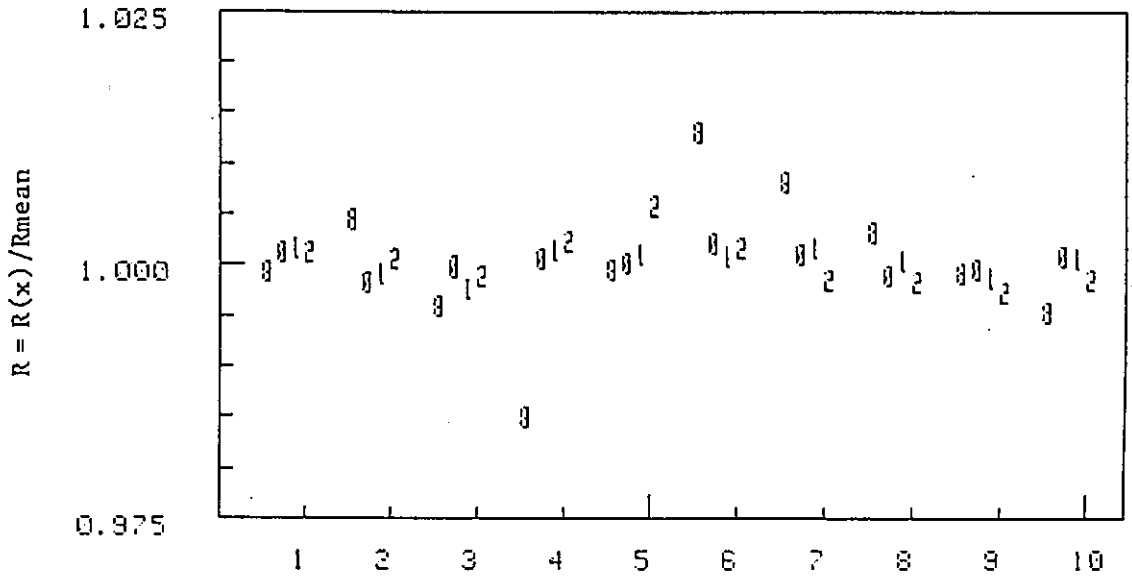
Total time spent on sample 30 mins 34 secs

Total time spent on all samples 1 hours 25.4 minutes

PNC Mass spec measurements Log # 7

Resin bead NBS 947 Pos #: 7





Resin bead Plutonium NBS 947 Log #: 7

PNC MASS SPECTROMETRIC ANALYSIS Instrument: VG-54E

Operator: Resin bead Date: 840221

Pos #	Log #	PNC id.	Type Code	Spike information	
7	7	NBS 947	4	0	0

N	238/239*	240/239*	241/239*	242/239	244/239*
1	.00366	.24095	.03281	.01532	.00001
2	.00368	.24024	.03273	.01530	.00001
3	.00365	.24061	.03267	.01528	.00000
4	.00361	.24081	.03280	.01533	.00001
5	.00366	.24068	.03279	.01538	.00001
6	.00371	.24117	.03278	.01532	.00001
7	.00369	.24091	.03281	.01527	.00000
8	.00367	.24039	.03276	.01527	.00001
9	.00366	.24054	.03271	.01525	.00001
10	.00364	.24085	.03277	.01527	.00000
Mean	.003663	.240716	.032764	.015300	.000006
Std	.000028	.000279	.000046	.000039	.000003
Rstd	.769932	.115716	.141103	.254878	47.541794

*) The printout does not represent the actual data taking

	238	239	240	241	242	244
Atom%	.28339	77.37258	18.62479	2.53500	1.18379	.00045
Std	.00218	.01715	.01802	.00353	.00299	.00021
Weight%	.28189	77.28523	18.68173	2.55337	1.19733	.00046

Atomic weight: 239.3223

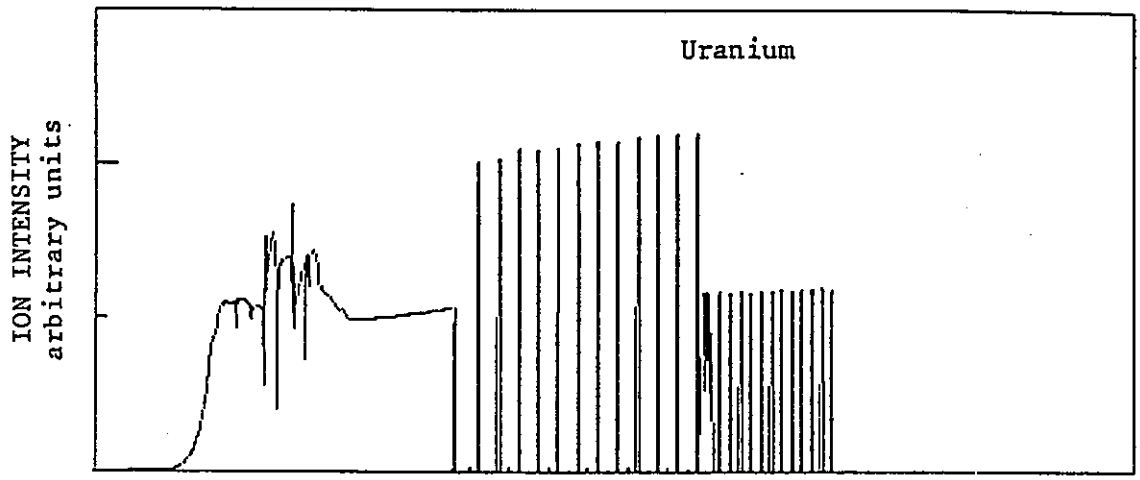
Filament current (A): 3.343

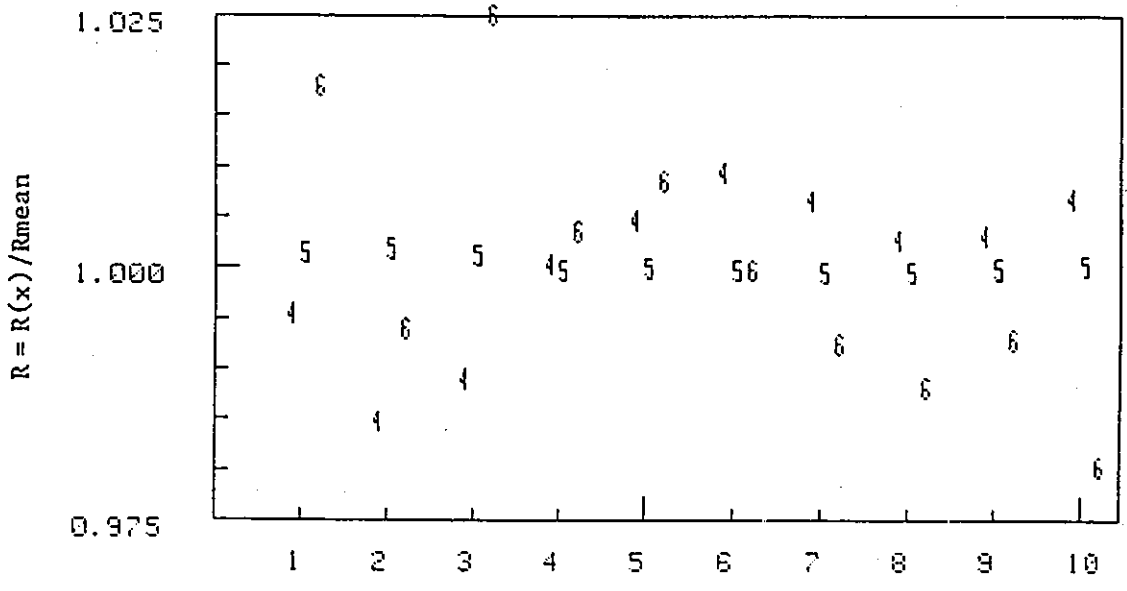
Average ion current of Plutonium: 22.1 E-14 amps

Total time spent on sample 41 mins 27 secs

PNC Mass spec measurements Log # 3

Resin bead NBS 500 Pos #: 3





Resin bead Uranium NBS 500 Log #: 3

PNC MASS SPECTROMETRIC ANALYSIS Instrument: VG-54E

Operator: R Resin bead Date: 840223

Pos #	Log #	PNC id.	Type Code	Spike information	
3	3	NBS 500	1	0	0

N	233/238	234/235*	235/238	236/235*
1	0.00000	.01042	1.00769	.00152
2	0.00000	.01031	1.00828	.00149
3	0.00000	.01036	1.00745	.00154
4	0.00000	.01048	1.00601	.00150
5	0.00000	.01052	1.00637	.00151
6	0.00000	.01057	1.00600	.00150
7	0.00000	.01054	1.00576	.00149
8	0.00000	.01050	1.00575	.00148
9	0.00000	.01051	1.00617	.00149
10	0.00000	.01054	1.00648	.00147
Mean	0.000000	.010476	1.006605	.001498
Std	0.000000	.000085	.000901	.000021
Rstd	0.000000	.810573	.089548	1.378272

*) The printout does not represent the actual data taking

	233	234	235	236	238
Atom%	0.00000	.52238	49.86505	.07471	49.53786
Std	0.00000	.00424	.03165	.00103	.02223
Weight%	0.00000	.51688	49.55197	.07456	49.85659

Atomic weight: 236.5290

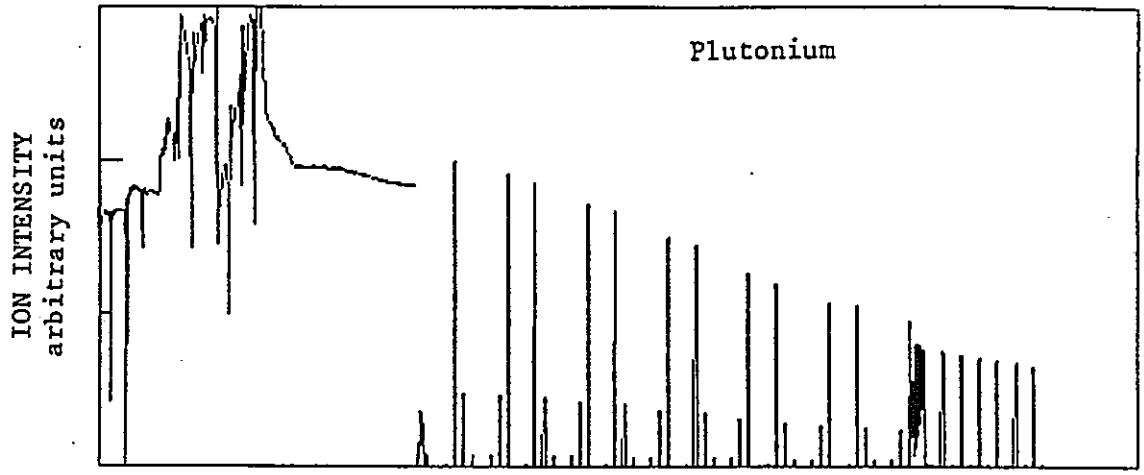
Filament current (A): 4.538

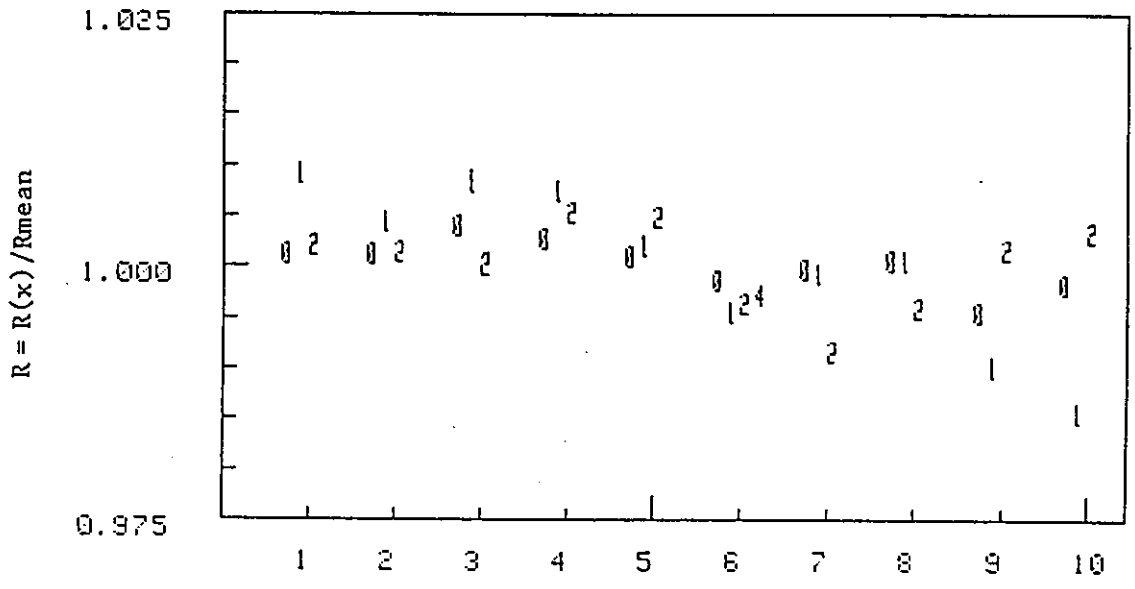
Average ion current of Uranium: 41.1 E-14 amps

Total time spent on sample 33 mins 6 secs

PNC Mass spec measurements Log # 15

Resin bead 947/500 Pos #: 15





Resin bead Plutonium 947/500 Log #: 15

PNC MASS SPECTROMETRIC ANALYSIS Instrument: VG-54E

Operator: R Resin bead Date: 840222

Pos #	Log #	PNC id.	Type Code	Spike information
15	15	947/500	4.1	0 0

N	238/239*	240/239*	241/239*	242/239	244/239*
1	.00505	.24084	.03480	.01551	.00002
2	.00518	.24084	.03464	.01550	.00000
3	.00533	.24151	.03478	.01549	-.00002
4	.00548	.24120	.03474	.01556	-.00001
5	.00562	.24078	.03456	.01556	-.00000
6	.00579	.24020	.03433	.01542	-.00000
7	.00595	.24049	.03446	.01535	0.00000
8	.00619	.24070	.03451	.01542	-.00000
9	.00649	.23947	.03414	.01551	-.00001
10	.00667	.24011	.03399	.01553	.00001
Mean	.005776	.240615	.034495	.015485	-.000002
Std	.000549	.000581	.000273	.000068	.000009
Rstd	9.499359	.241444	.790015	.441727	-581.019593

*) The printout does not represent the actual data taking

	238	239	240	241	242	244
Atom%	.44558	77.13844	18.56069	2.66090	1.19452	-.00012
Std	.04214	.05041	.03846	.02054	.00527	-.00072
Weight%	.44321	77.05118	18.61739	2.68018	1.20817	-.00013

Atomic weight: 239.3228

Mixed bead, U-238 interference on Pu-238, final values on Uranium printout

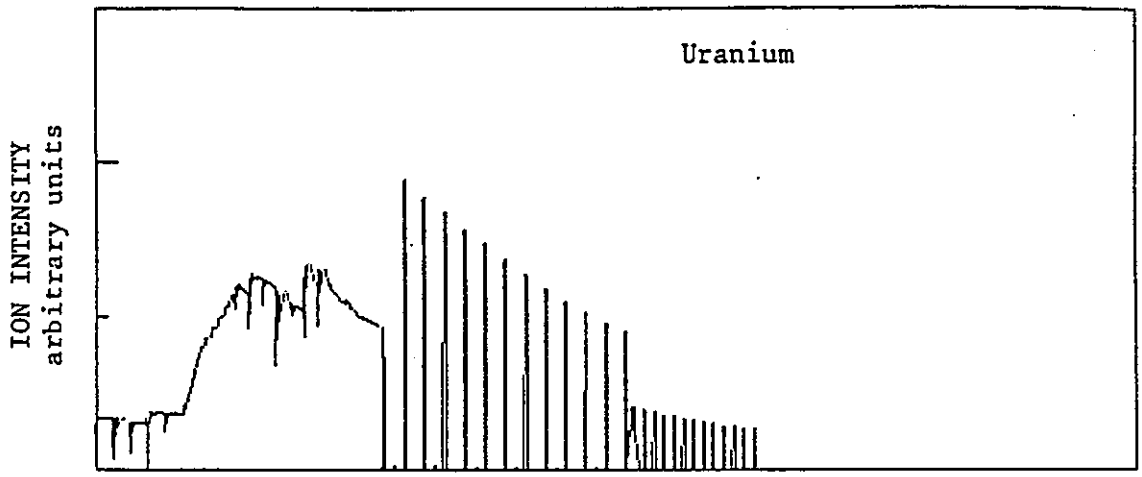
Filament current (A): 2.959

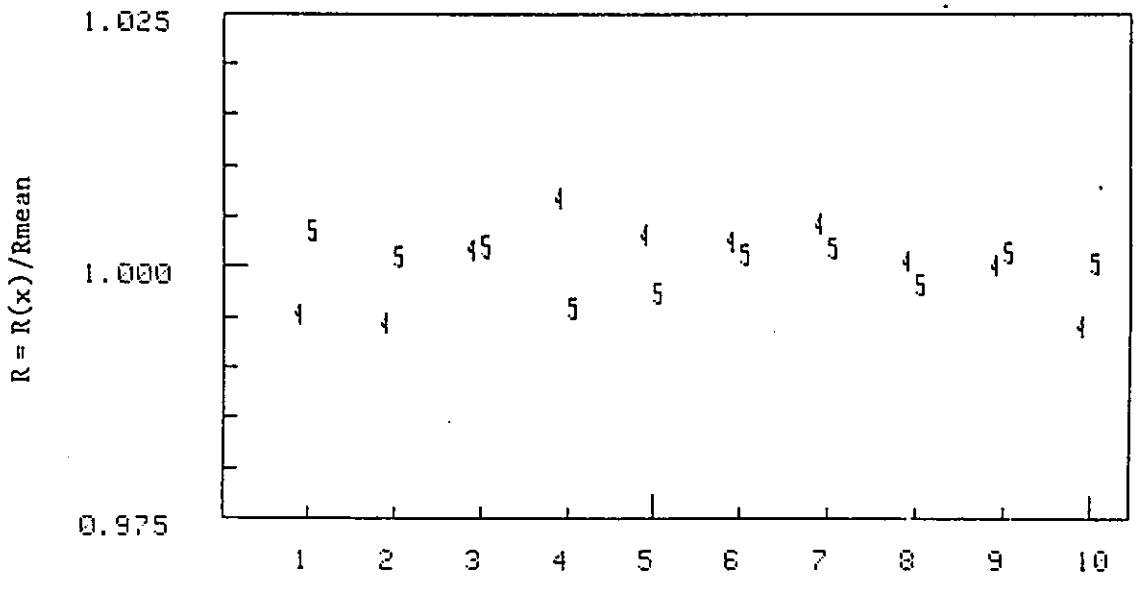
Average ion current of Plutonium: 16.8 E-14 amps

Total time spent on sample 44 mins 28 secs

PNC Mass spec measurements Log # 15

Resin bead 947/500 Pos #: 15





Resin bead Uranium 947/500 Log #: 15

PNC MASS SPECTROMETRIC ANALYSIS Instrument: VG-54E

Operator: R Resin bead Date: 840222

Pos #	Log #	PNC id.	Type Code	Spike information
15	15	947/500	4.1	0 0

N	233/238	234/235*	235/238	236/235*
1	0.00000	.01039	.98608	.00135
2	0.00000	.01038	.98355	.00152
3	0.00000	.01045	.98459	.00133
4	0.00000	.01050	.97866	.00152
5	0.00000	.01047	.97999	.00134
6	0.00000	.01046	.98384	.00153
7	0.00000	.01048	.98454	.00138
8	0.00000	.01044	.98083	.00157
9	0.00000	.01044	.98402	.00132
10	0.00000	.01037	.98304	.00156
Mean	0.000000	.010437	.982914	.001441
Std	0.000000	.000046	.002332	.000107
Rstd	0.000000	.436753	.237260	7.417237

*) The printout does not represent the actual data taking

	233	234	235	236	238
Atom%	0.00000	.51435	49.27901	.07101	50.13564
Std	0.00000	.00261	.08273	.00527	.05869
Weight%	0.00000	.50890	48.96588	.07086	50.45437

Atomic weight: 236.5470

Burn off time for Pu: 3 min & 51 secs

Recalculated isotopic of Plutonium

	238	239	240	241	242	244
Atom%	.30074	77.25066	18.58769	2.66477	1.19626	-.00012

Filament current (A): 4.060

Average ion current of Uranium: 28.5 E-14 amps

Total time spent on sample 30 mins 30 secs

*** NOTE Pos #: 14 no Plutonium peak found -----> ABORTED

Log #: 14 PNC-identification: 947/500

Use the following CODES for RESIN BEADS:

URANIUM : -> 1 U-beads, -> 2 U-spiked beads

PLUTONIUM: -> 4 Pu-beads, -> 5 Pu-242 spiked, -> 6 Pu-244 spiked beads

MIXED BEADS: -> 4.1 U-Pu -> 5.2 U/Pu-242 spiked,
-> 6.2 U/Pu-244 spiked beads

PNC MASS SPECTROMETRIC ANALYSIS Instrument: VG-54E

Operator: R Resin bead Date: 840222

Pos #	Log #	PNC id.	Type Code	Spike information	
1	1		0.0	0.00000	0.00000
2	2		0.0	0.00000	0.00000
3	3		0.0	0.00000	0.00000
4	4		0.0	0.00000	0.00000
5	5		0.0	0.00000	0.00000
6	6		0.0	0.00000	0.00000
7	7		0.0	0.00000	0.00000
8	8		0.0	0.00000	0.00000
9	9		0.0	0.00000	0.00000
10	10		0.0	0.00000	0.00000
11	11		0.0	0.00000	0.00000
12	12		0.0	0.00000	0.00000
13	13		0.0	0.00000	0.00000
14	14		0.0	0.00000	0.00000
15	15	947/500	4.1	0.00000	0.00000
16	16	947/500	4.1	0.00000	0.00000

Measurements start with position: 15

Log #: 16 947/500 Date: 84022 mixed bead load

	233	234	235	236	238	U tot
Atom percent:	0.0000	.5198	49.6979	.0743	49.7080	0.0000
Weight percent:	0.0000	.5143	49.3848	.0741	50.0268	0.0000
Atomic weight:	236.5341					

Log #: 16 947/500 Date: 84022 mixed bead load

	238	239	240	241	242	244	Pu tot
Atom percent:	-.6571	78.4048	18.5366	2.5258	1.1893	.0005	0.0000
Weight percent:	-.6536	78.3135	18.5926	2.5440	1.2029	.005	
Atomic weight:	239.3309						

Log #: 16 947/500 Date: 84022 mixed bead load

	238	239	240	241	242	244	Pu tot
Atom percent:	-.6571	78.4048	18.5366	2.5258	1.1893	.0005	0.0000
Weight percent:	-.6536	78.3135	18.5926	2.5440	1.2029	.0005	
Atomic weight:	239.3309						

VARIABLES USED IN PROGRAM * BEADS * file -----> Varb

1	1st pretreat current, Pu	: 1.2
2	2nd pretreat current, Pu	: 1.5
3	1st pretreat current, U	: 1.5
4	2nd pretreat current, U	: 2.8
5	Initial current , Pu	: 2.95
6	Initial current , U	: 3.8
7	Increment current , Pu	: .05
8	Increment current , U	: .1
9	Limit current , Pu	: 4.2
10	Limit current , U	: 5
11	1=FARADAY CUP, 0=MULTIPIER	: 0
12	Limit ion current , Pu	: 200000
13	Limit ion current , U	: 350000
14	Scan value	: 60
15	Mass discr. (non mixed bead)	: 0
16	Mass discr. (mixed bead U)	: 0

$OMW?O
$OMW?O

Use the following CODES for RESIN BEADS:

URANIUM : -> 1 U-beads, -> 2 U-spiked beads

PLUTONIUM: -> 4 Pu-beads, -> 5 Pu-242 spiked, -> 6 Pu-244 spiked beads

MIXED BEADS: -> 4.1 U/Pu -> 5.2 U/Pu-242 spiked,
-> 6.2 U/Pu-244 spiked beads

PNC MASS SPECTROMETRIC ANALYSIS Instrument: VG-54E

NAME PRO TYPE REC/FILE BYTES/REC ADDRESS
T14 2

840222 DATA 256 5

Use the following CODES for RESIN BEADS:

URANIUM : -> 1 U-beads, -> 2 U-spiked beads

PLUTONIUM: -> 4 Pu-beads, -> 5 Pu-242 spiked, -> 6 Pu-244 spiked beads

MIXED BEADS: -> 4.1 U/Pu -> 5.2 U/Pu-242 spiked,
-> 6.2 U/Pu-244 spiked beads

PNC MASS SPECTROMETRIC ANALYSIS Instrument: VG-54E

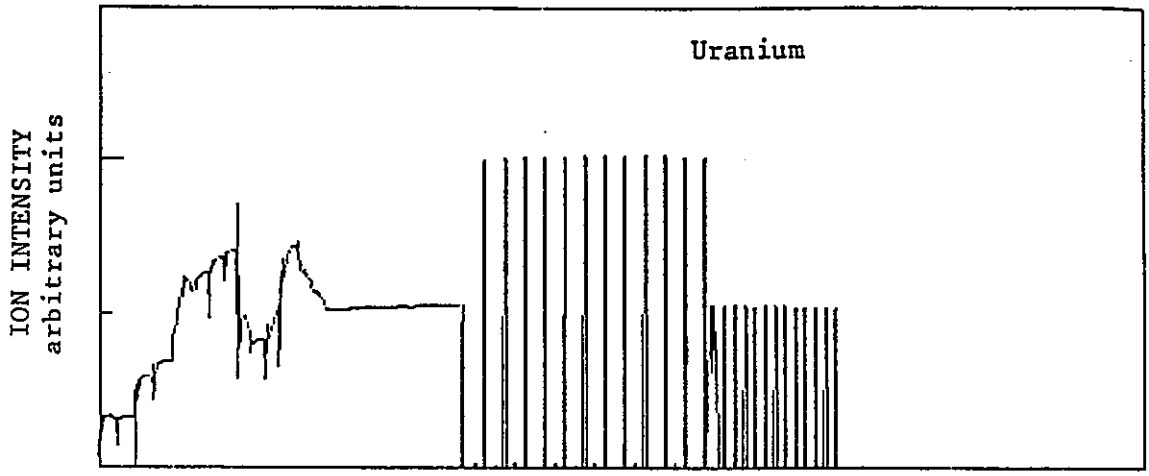
Operator: R Resin bead Date: 840223

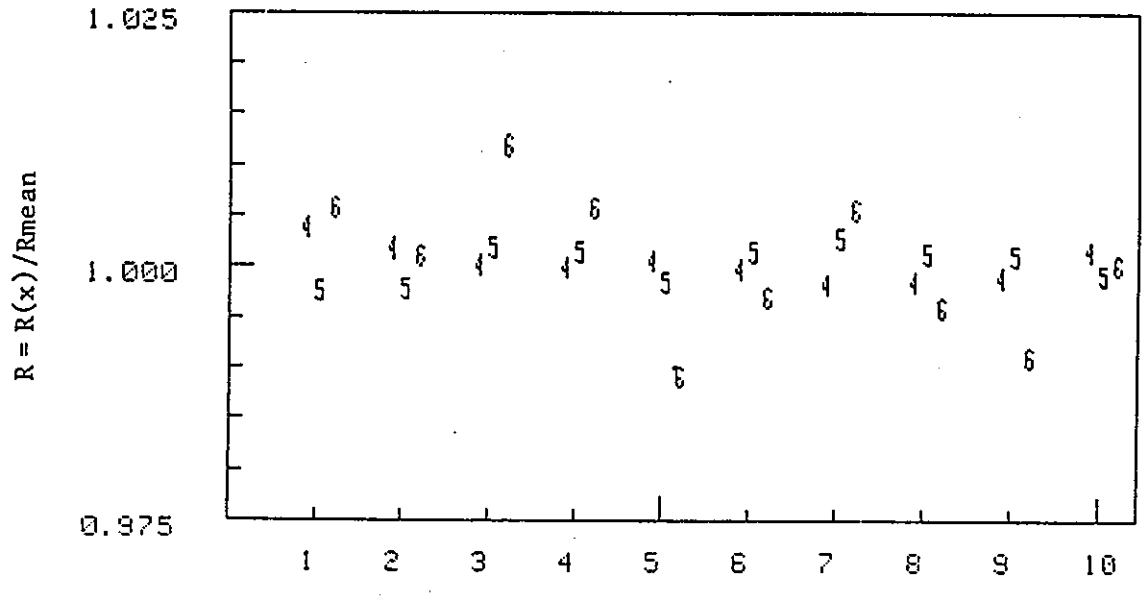
Pos #	Log #	PNC id.	Type Code	Spike information	
1	1		0.0	0.00000	0.00000
2	2		0.0	0.00000	0.00000
3	3	NBS 500	1.0	0.00000	0.00000
4	4	NBS 500	1.0	0.00000	0.00000
5	5		0.0	0.00000	0.00000
6	6	NBS 930	1.0	0.00000	0.00000
7	7		0.0	0.00000	0.00000
8	8	NBS 947	4.0	0.00000	0.00000
9	9	NBS 947	4.0	0.00000	0.00000
10	10		0.0	0.00000	0.00000
11	11		0.0	0.00000	0.00000
12	12		0.0	0.00000	0.00000
13	13		0.0	0.00000	0.00000
14	14		0.0	0.00000	0.00000
15	15		0.0	0.00000	0.00000
16	16		0.0	0.00000	0.00000

Measurements start with position: 3

PNC Mass spec measurements Log # 4

Resin bead NBS 500 Pos #: 4





Resin bead Uranium NBS 500 Log #: 4

PNC MASS SPECTROMETRIC ANALYSIS Instrument: VG-54E

Operator: R Resin bead Date: 840223

Pos #	Log #	PNC id.	Type Code	Spike information	
4	4	NBS 500	1	0	0

N	233/238	234/235*	235/238	236/235*
1	0.00000	.01050	.99995	.00150
2	0.00000	.01048	1.00025	.00149
3	0.00000	.01047	1.00441	.00151
4	0.00000	.01046	1.00395	.00150
5	0.00000	.01047	1.00090	.00147
6	0.00000	.01046	1.00398	.00148
7	0.00000	.01045	1.00511	.00150
8	0.00000	.01045	1.00361	.00148
9	0.00000	.01045	1.00347	.00148
10	0.00000	.01048	1.00162	.00149
Mean	0.000000	.010467	1.002725	.001489
Std	0.000000	.000018	.001864	.000011
Rstd	0.000000	.172934	.185940	.720294

*) The printout does not represent the actual data taking

	233	234	235	236	238
Atom%	0.00000	.52096	49.77010	.07411	49.63483
Std	0.00000	.00140	.06544	.00056	.04594
Weight%	0.00000	.51547	49.45700	.07396	49.95357

Atomic weight: 236.5319

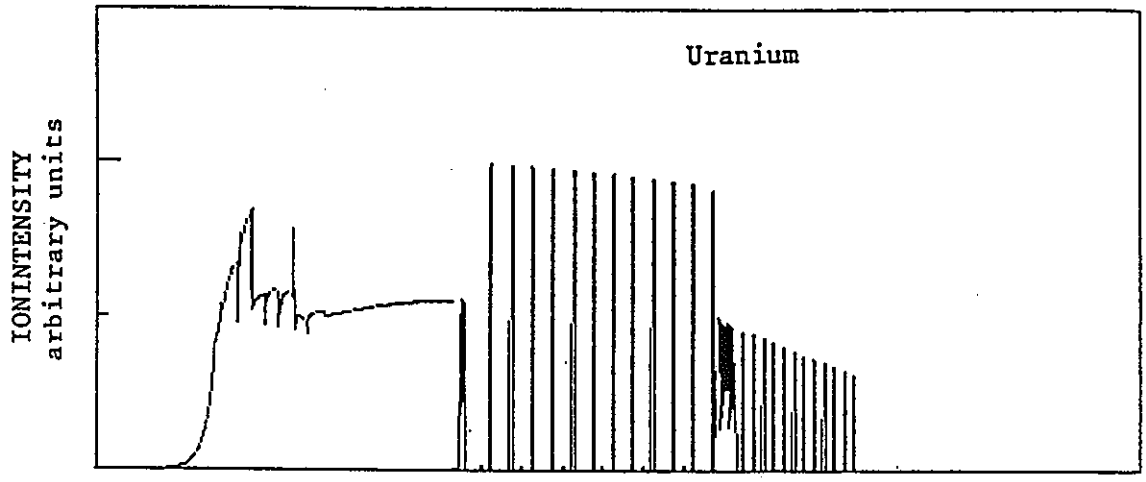
Filament current (A): 3.715

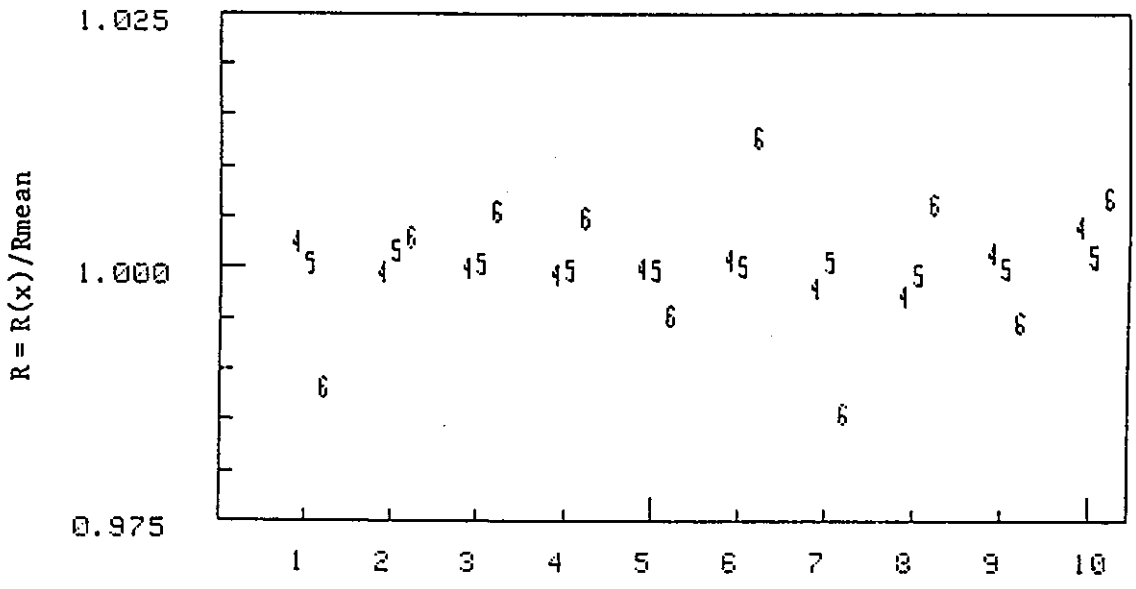
Average ion current of Uranium: 37.0 E-14 amps

Total time spent on sample 33 mins 0 secs

PNC Mass spec measurements Log # 2

Resin bead NBS 500 Pos #: 2





Resin bead Uranium NBS 500 Log #: 2

PNC MASS SPECTROMETRIC ANALYSIS Instrument: VG-54E

Operator: Resin bead Date: 840221

Pos #	Log #	PNC id.	Type Code	Spike information	
2	2	NBS 500	1	0	0

N	233/238	234/235*	235/238	236/235*
1	0.00000	.01050	.99989	.00146
2	0.00000	.01047	1.00110	.00148
3	0.00000	.01048	.99990	.00149
4	0.00000	.01047	.99925	.00149
5	0.00000	.01048	.99930	.00147
6	0.00000	.01049	.99964	.00150
7	0.00000	.01046	1.00011	.00146
8	0.00000	.01045	.99874	.00149
9	0.00000	.01049	.99943	.00147
10	0.00000	.01052	1.00065	.00149
Mean	0.000000	.010480	.999800	.001480
Std	0.000000	.000021	.000698	.000013
Rstd	0.000000	.198729	.069776	.888638

*) The printout does not represent the actual data taking

	233	234	235	236	238
Atom%	0.00000	.52085	49.69782	.07357	49.70775
Std	0.00000	.00111	.02453	.00066	.01725
Weight%	0.00000	.51536	49.38472	.07342	50.02649

Atomic weight: 236.5341

Filament current (A): 4.633

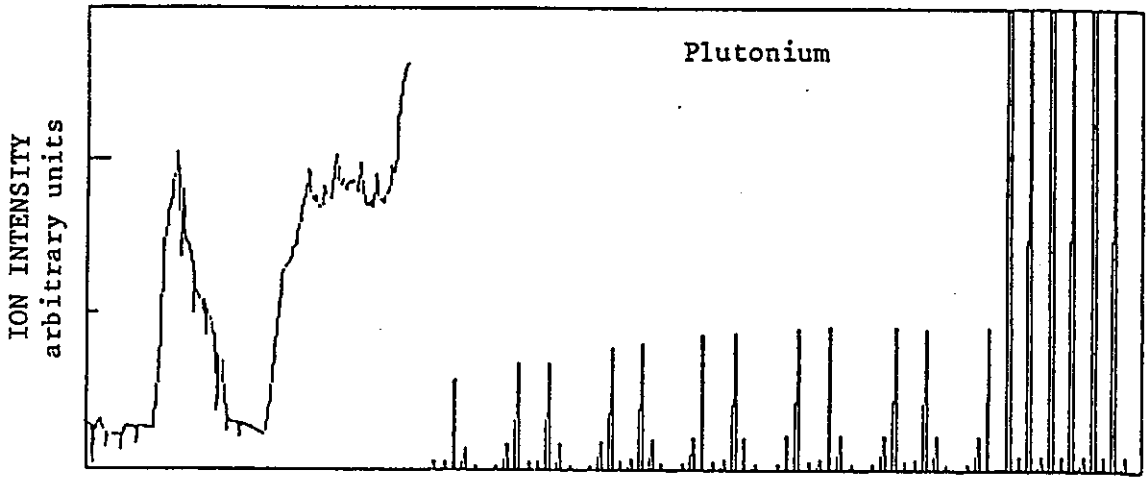
Average ion current of Uranium: 27.8 E-14 amps

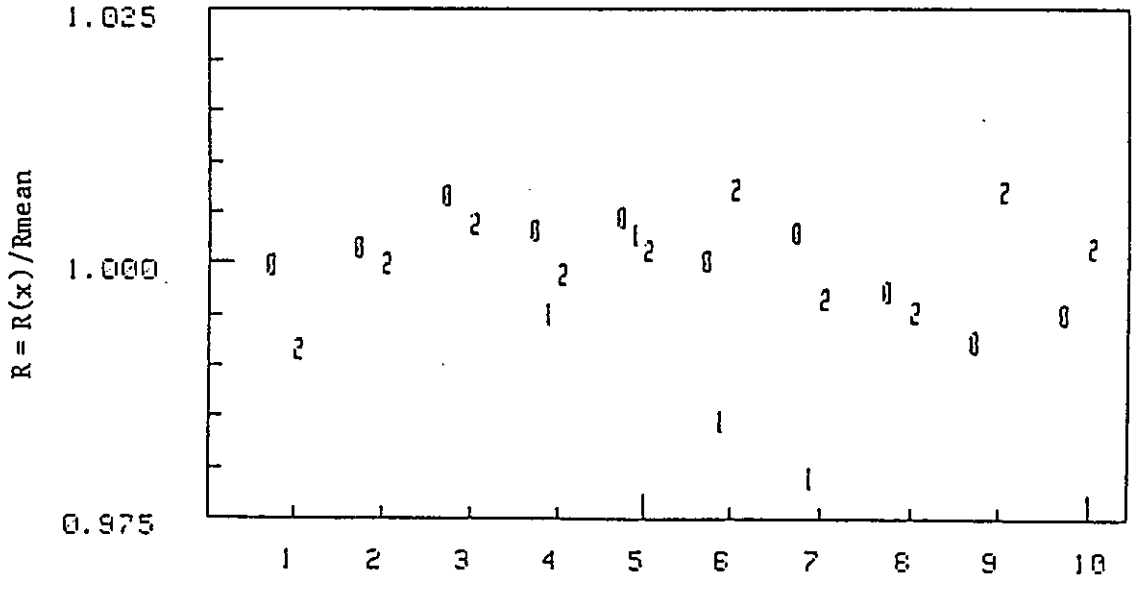
Total time spent on sample 33 mins 47 secs

The Results of JAERI [Attachment 3]

JAERI Mass spec measurements Log # 2

Resin bead 947/500 Pos #: 2





Resin bead Plutonium 947/500 Log #: 2

JAERI MASS SPECTROMETRIC ANALYSIS Instrument: IM-54E-38

Operator: F Resin bead Date: 840221

Pos #	Log #	JAERI id.	Type Code	Spike information	
2	2	947/500	4.1	0	0

N	238/239*	240/239*	241/239*	242/239	244/239*
1	.09252	.24066	.04137	.01536	-.00000
2	.00599	.24108	.04022	.01549	-.00000
3	.08106	.24232	.03863	.01555	-.00000
4	.07532	.24149	.03772	.01548	-.00000
5	.07145	.24181	.03801	.01551	-.00000
6	.06882	.24077	.03732	.01561	-.00000
7	.06758	.24143	.03711	.01544	-.00000
8	.06600	.24007	.03670	.01542	-.00001
9	.06570	.23890	.03633	.01560	-.00001
10	.06660	.23955	.03576	.01552	-.00000
Mean	.07106	.240808	.037919	.015498	-.000004
Std	.009431	.001055	.001746	.000078	.000001
Rstd	12.726782	.438307	4.603665	.501646	-32.080175

*) The printout does not represent the actual data taking

	238	239	240	241	242	244
Atom%	5.41580	73.08200	17.59869	2.77118	1.13259	-.00027
Std	.65305	.51539	.13944	.12557	.00976	-.00009
Weight%	5.38832	73.01737	17.65682	2.79195	1.14582	-.00028

Atomic weight: 239.2637

Mixed bead, U-238 interference on Pu-238, final values on Uranium printout

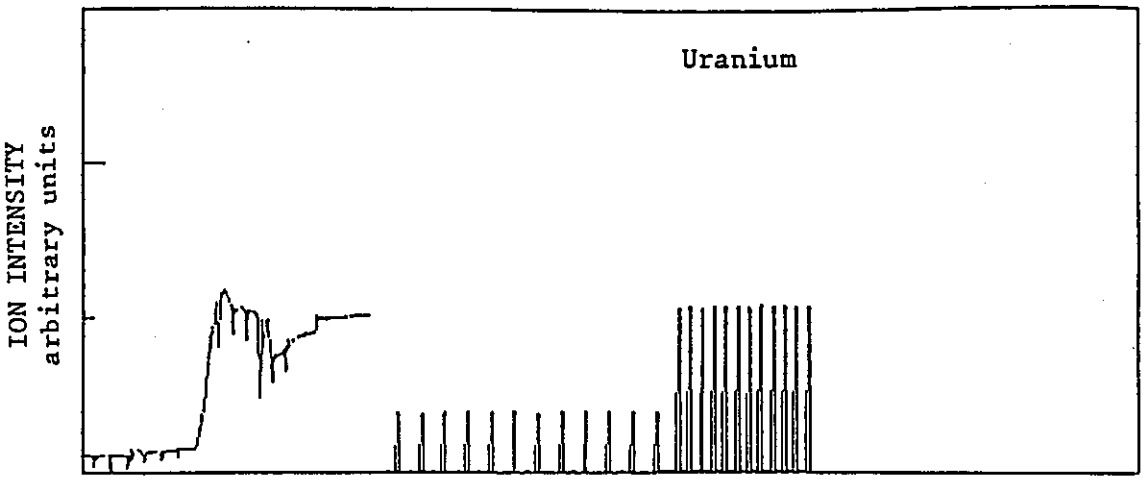
Filament current (A): 3.348

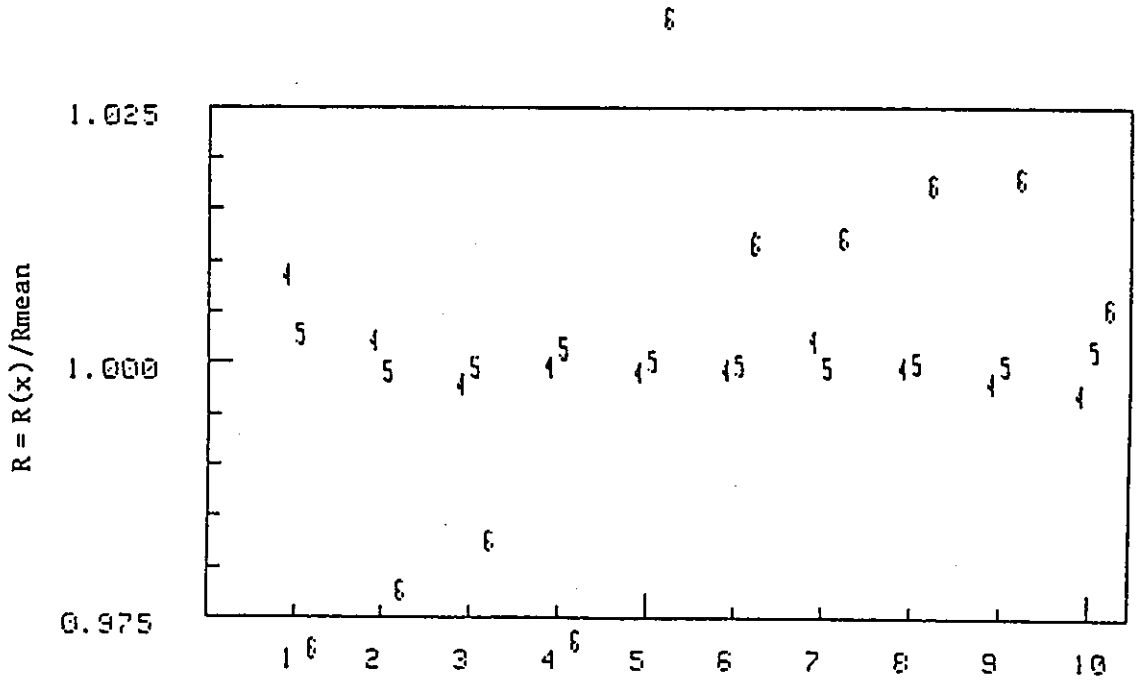
Average ion current of Plutonium: 54.5 E-14 amps

Total time spent on sample 47 mins 36 secs

JAERI Mass spec measurements Log # 2

Resin bead 947/500 Pos #: 2





Resin bead Uranium 947/500 Log #: 2

JAERI MASS SPECTROMETRIC ANALYSIS Instrument: IM-54E-38

Operator: F Resin bead Date: 840221

Pos #	Log #	JAERI id.	Type Code	Spike information	
2	2	947/500	4.1	0	0

N	233/238	234/235*	235/238	236/235*
1	0.00000	.01058	.99206	.00146
2	0.00000	.01051	.98838	.00147
3	0.00000	.01047	.98877	.00147
4	0.00000	.01049	.99865	.00146
5	0.00000	.01048	.98946	.00155
6	0.00000	.01048	.98907	.00152
7	0.00000	.01051	.98876	.00152
8	0.00000	.01049	.98917	.00153
9	0.00000	.01047	.98909	.00153
10	0.00000	.01046	.99052	.00151
Mean	0.000000	.010495	.989592	.001501
Std	0.000000	.000035	.001137	.000033
Rstd	0.000000	.334536	.114876	2.208244

*) The printout does not represent the actual data taking

	233	234	235	236	238
Atom%	0.00000	.51889	49.44345	.07421	49.96345
Std	0.00000	.00185	.04018	.00164	.02841
Weight%	0.00000	.51341	49.13035	.07405	50.28219

Atomic weight: 236.5418

Burn off time for Pu: 3 min & 51 secs

Recalculated isotopic of Plutonium

	238	239	240	241	242	244
Atom%	.17532	77.13115	18.57376	2.92472	1.19534	-.00029

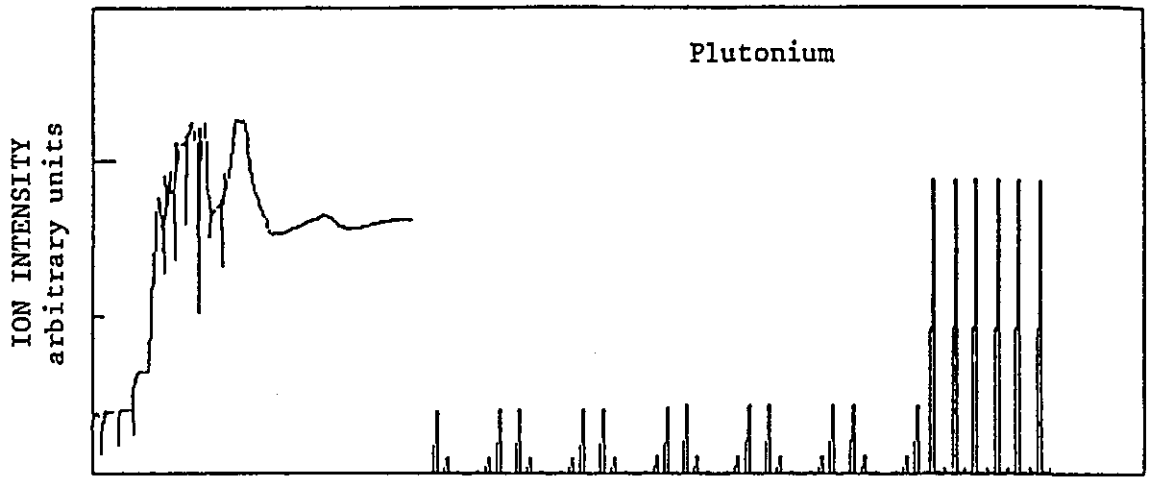
Filament current (A): 3.553

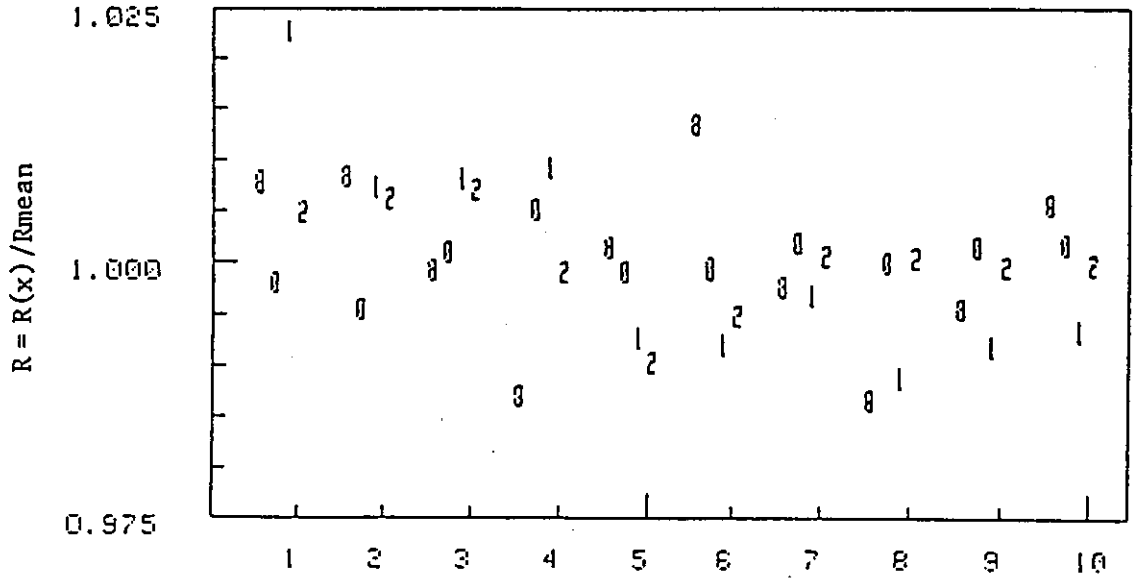
Average ion current of Uranium: 73.9 E-14 amps

Total time spent on sample 32 mins 24 secs

JAERI Mass spec measurements Log # 4

Resin bead NBS 947 Pos #: 4





Resin bead Plutonium NBS 947 Log #: 4

JAERI MASS SPECTROMETRIC ANALYSIS Instrument: IM-54E-38

Operator: F Resin bead Date: 840221

Pos #	Log #	JAERI id.	Type Code	Spike information	
4	4	NBS 947	4	0	0

N	238/239*	240/239*	241/239*	242/239	244/239*
1	.00352	.24038	.03415	.01559	-.00000
2	.00352	.23978	.03363	.01561	.00001
3	.00349	.24111	.03366	.01562	.00002
4	.00345	.24213	.03369	.01550	.00001
5	.00350	.24065	.03314	.01536	-.00000
6	.00354	.24074	.03312	.01543	-.00000
7	.00348	.24131	.03328	.01552	.00000
8	.00345	.24084	.03302	.01552	.00000
9	.00348	.24121	.03311	.01551	.00000
10	.00351	.24129	.03316	.01551	-.00001
Mean	.003494	.240943	.033395	.015517	.000002
Std	.000031	.000628	.000366	.000079	.000006
Rstd	.892417	.260768	1.096575	.506886	368.194483

*) The printout does not represent the actual data taking

	238	239	240	241	242	244
Atom%	.27015	77.31846	18.62938	2.58209	1.19978	.00014
Std	.00241	.04377	.04091	.02762	.00605	.00050
Weight%	.26872	77.23067	18.68621	2.60078	1.21349	.00014

Atomic weight: 239.3239

Filament current (A): 2.560

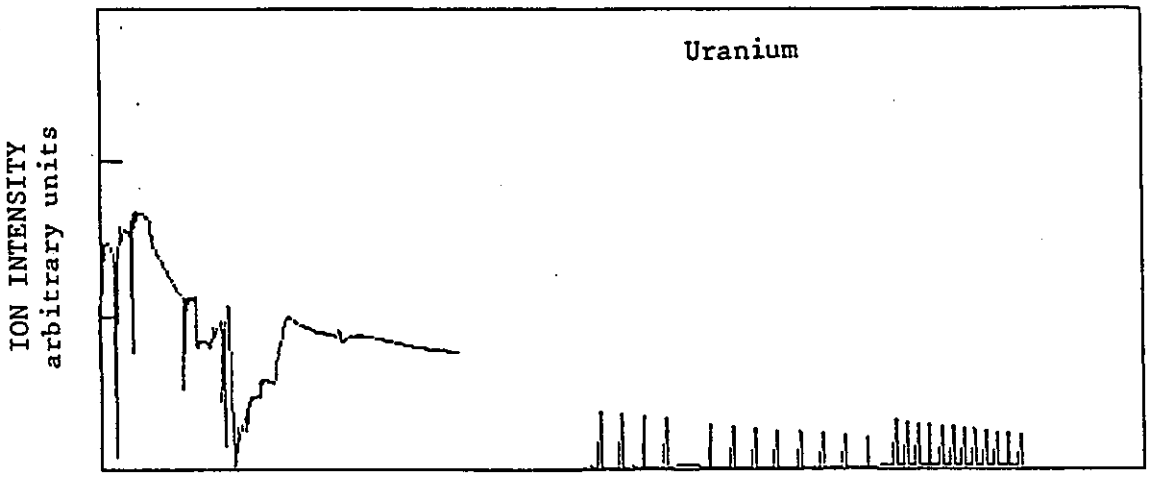
Average ion current of Plutonium: 17.9 E-14 amps

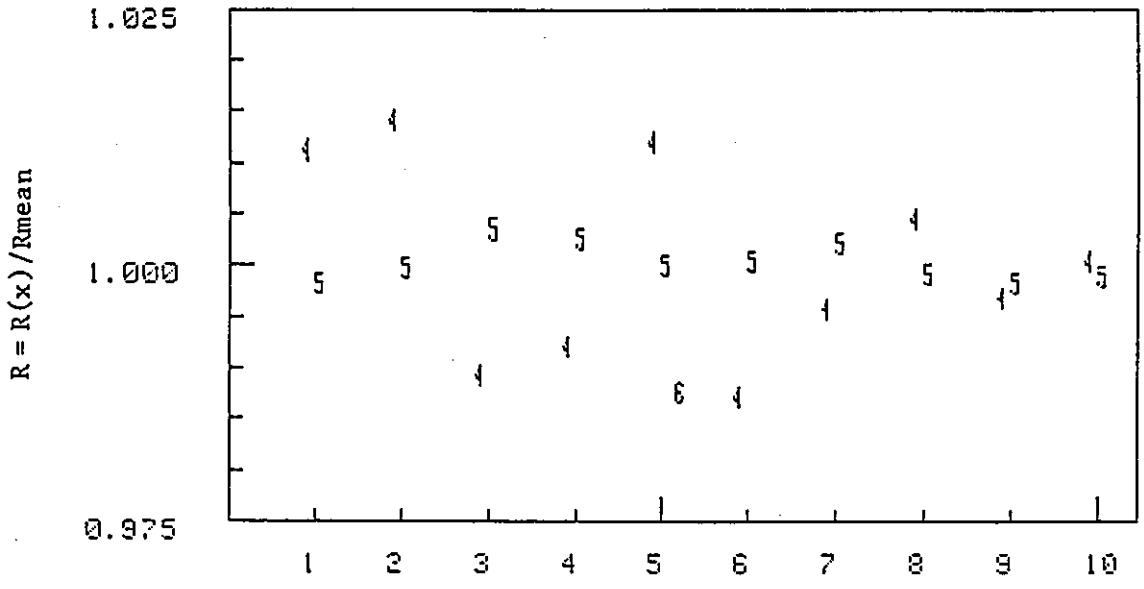
Total time spent on sample 44 mins 34 secs

The Results of NMCC [Attachment 4]

NMCC Mass spec measurements Log # 4

Resin bead NBS 500 Pos #: 4





6

Resin bead Uranium NBS 500 Log #: 4

NMCC MASS SPECTROMETRIC ANALYSIS Instrument: MM-30

Operator: R Resin bead Date: 820221

Pos #	Log #	NMCC id.	Type Code	Spike information	
4	4	NBS 500	1	0	0

N	233/238	234/235*	235/238	236/235*
1	0.00000	.01058	.99861	.00135
2	0.00000	.01061	1.00024	.00153
3	0.00000	.01035	1.00396	.00131
4	0.00000	.01038	1.00309	.00153
5	0.00000	.01059	1.00047	.00143
6	0.00000	.01033	1.00090	.00157
7	0.00000	.01042	1.00247	.00138
8	0.00000	.01051	.99951	.00156
9	0.00000	.01043	.99876	.00132
10	0.00000	.01047	.99943	.00151
Mean	0.000000	.010465	1.000745	.001450
Std	0.000000	.000102	.001853	.000101
Rstd	0.00000	.978978	.185131	7.001075

*) The printout does not represent the actual data taking

	233	234	235	236	238
Atom%	0.00000	.52035	49.72229	.07207	49.68528
Std	0.00000	.00518	.06519	.00504	.04588
Weight%	0.00000	.51487	49.40918	.07192	50.00402

Atomic weight: 236.5334

Filament current (A): 3.743

Average ion current of Uranium: 10.2 E-14 amps

Total time spent on sample 39 mins 25 secs

ATTACHMENT 2

Invitation schedule for Mr.R.Fielder, staff of the IAEA-SAL

Key objectives: Debugging and demonstration of the resin bead measurement program developed by the IAEA. : Preparation of resin bead samples (JASPAS JC-4)

Feb.

13th Travel to PNC Tokai Works

Technical meetings [PNC, JAERI, NMCC]

- JASPAS JC-4; on preparation of resin beads etc.
- on TIGR 82 and 84; problems on resin bead measurement
- confirmation of contents worked out this time

14th PNC/TRP-Analysis (PNC/FCTDD-Analysis)

↓ • debugging of software for resin bead measurement

18th • demonstration of software for resin bead measurement

- preparation technique for resin bead samples
- resin bead mounting ┐
  ├ training
- resin bead measurement ┘

20th JAERI

↓ NMCC

22nd • debugging of software for resin bead measurement

- demonstration of software for resin bead measurement
- others

23rd Technical meetings (PNC, JAER, NMCC)

Preparation of reports

24th Travel to Tokyo

Report to STA

[3] Technical Development of Sample Preparation

1. Installation of Glove Boxes for Resin Bead Sampling

1-1. Introduction

The samples of uranium and plutonium contained in feed-accounting solutions (spent-fuel-dissolved solutions) are prepared by the resin bead technique, which is accompanied by the problems such as (1)great effect of contamination due to the trace amounts of uranium and plutonium adsorbed by resin beads and (2) difficult handling of resin beads because of their fineness; accordingly, the preparation of resin beads in ordinary facilities and installations were difficult.

In order to make the preparation of resin bead samples easy and improve the accuracy of analysis by solving these problems, a glove box line exclusive for resin bead sampling was manufactured and in October, 1983 installed in the High-level Radioactive Sample Analysis Room (G 105) located in the first floor of the Analysis Laboratory of the PNC/TRP. The glove box line consists of 2 SUS glove boxes (one of them is lead-shielded) and one fume hood. Each box is connected with each other by a tunnel port.

In the lead-shielded glove box, a feed-accounting sample is received, sample solution is taken and adsorption by a resin bead is carried out. In the next glove box, the resin bead is washed and dried. In the fume hood, the contamination of the resin bead is inspected and taken out from the hood as the sample for safeguards analysis.

1-2. Place of Installation

The glove box line was installed in the High-level Radioactive Sample Analysis Room (G 105) located in the first floor of the Analysis Laboratory of the PNC/TRP (See Fig.1).

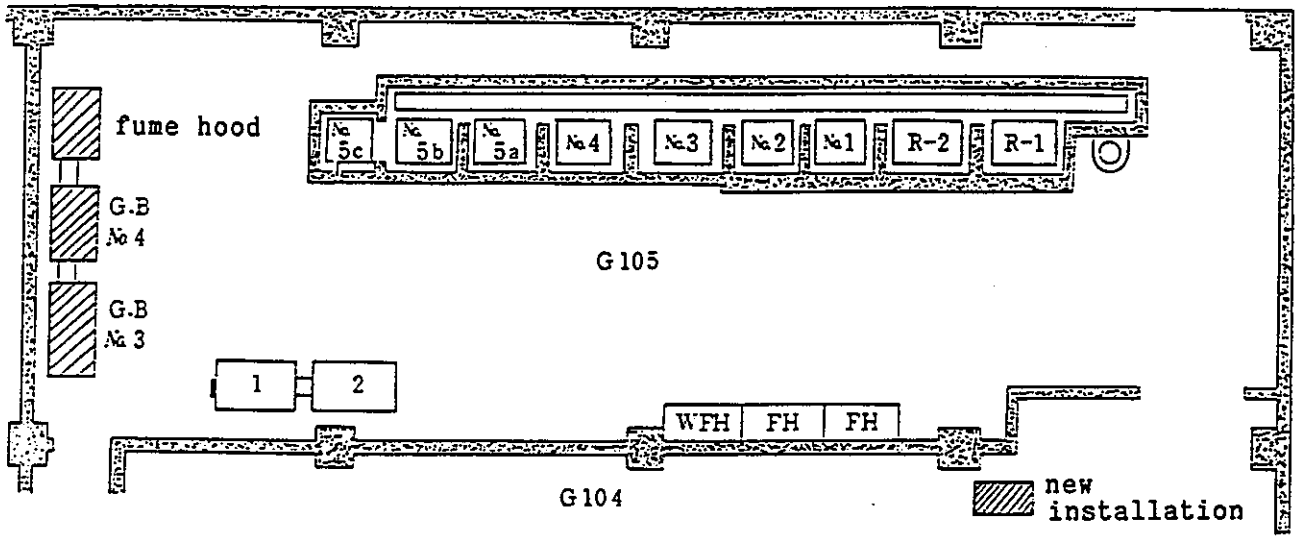


Fig.1 High-level Sample Analysis Room (G 105) for accountancy

1-3. Structures and Dimensions of Glove Boxes

The structures and dimensions of the glove boxes and the fume hood are shown in Table 1 and Fig.s 2 to 4.

Table 2 Structures,dimensions etc. of glove boxes and fume hood

Name	Material	Dimensions (m) length*width*height	Remarks
Shielded glove box	SUS304L,lead lead glass acrylic plate	0.8 * 1.3 * 1.8	See Fig.2
Glove box	SUS304L, lead glass acrylic plate	0.8 * 1.3 * 1.8	See Fig.3
Fume hood	SUS304L acrylic plate	0.8 * 1.3 * 1.8	See Fig.4

(1) Shielded Glove Box

negative pressure : -20mm H_2O/cm^2 or more

air tightness : 0.5 vol %/hr or less

Accessories

control panel (with a negative pressure meter and an alarm set at −5 mm H_2O/cm^2)

reagent bottle (including PVC* piping and nick)

ball-and-socket-type manipulator (ball and socket: SS)

pneumatic piping (material: SUS304)

Note : * vinyl chloride

(Analytical procedure)

sample receiving and shipping

sample taking

adsorption of nuclear materials by resin beads

(2) Glove Box without Shielding

negative pressure : -20mm H_2O/cm^2 or more

air tightness : 0.5 vol %/hr or less

Accessories

control panel (with a negative pressure meter and an alarm set at −5 mm H_2O/cm^2)

reagent bottle (including PVC piping and nick)

(Analytical procedure)

washing and drying of resin beads

1-4. Results

The glove box line for resin bead sampling was installed, and has been used for preparing samples since the fifth joint experiment. This measure eliminated the contamination of resin beads, improved work ability and reduced the exposure of operators during working.

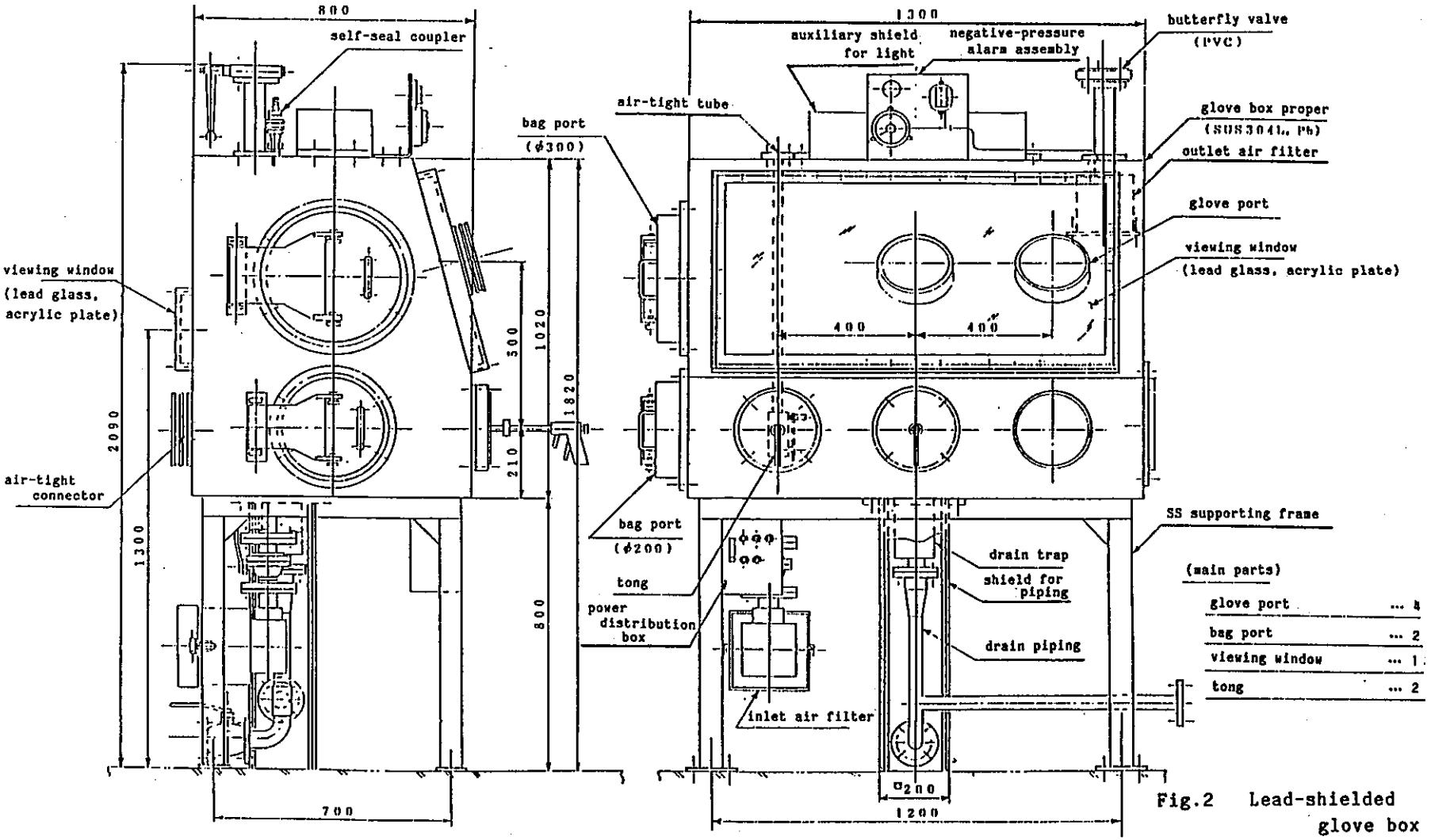


Fig.2 Lead-shielded glove box

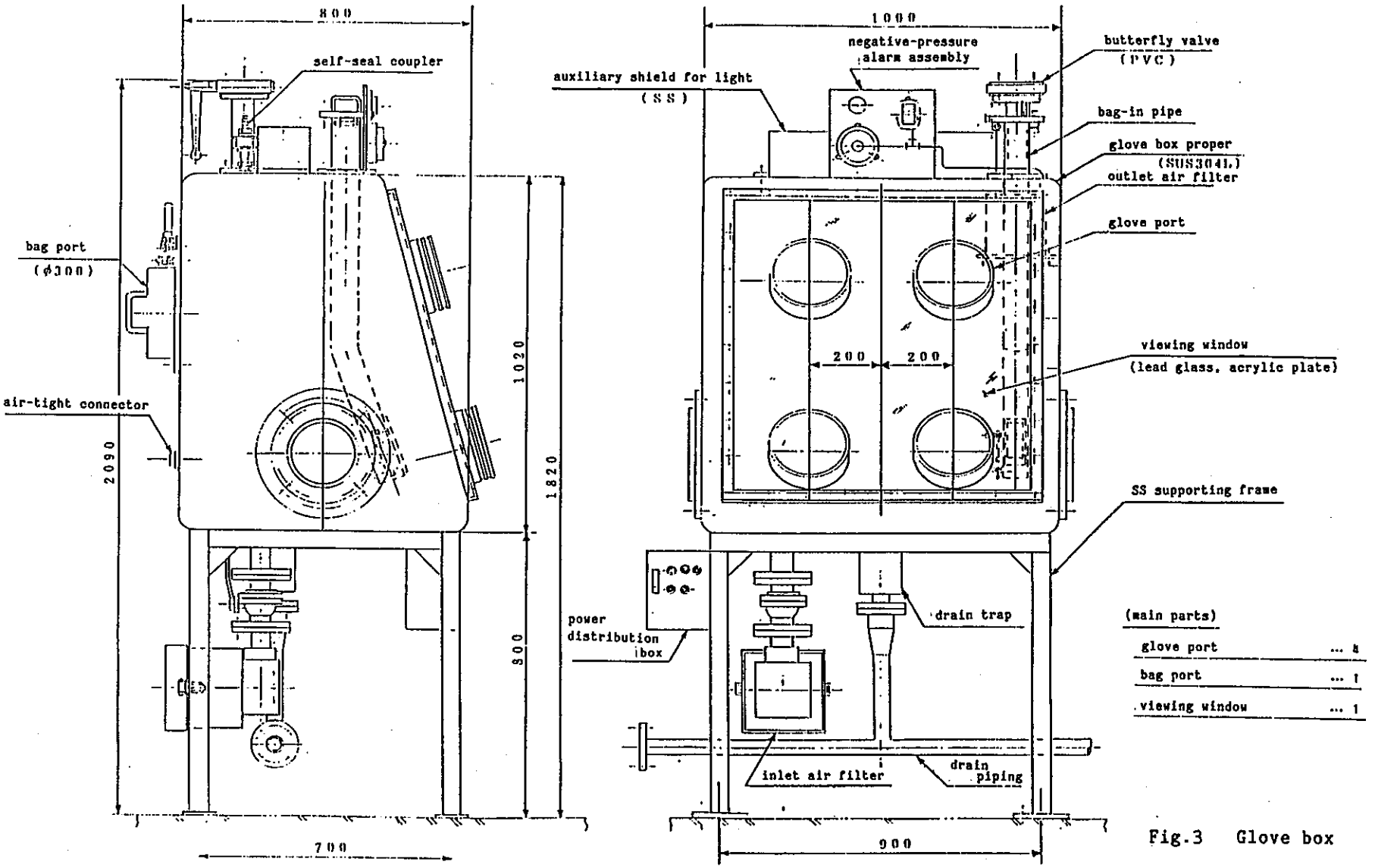


Fig.3 Glove box

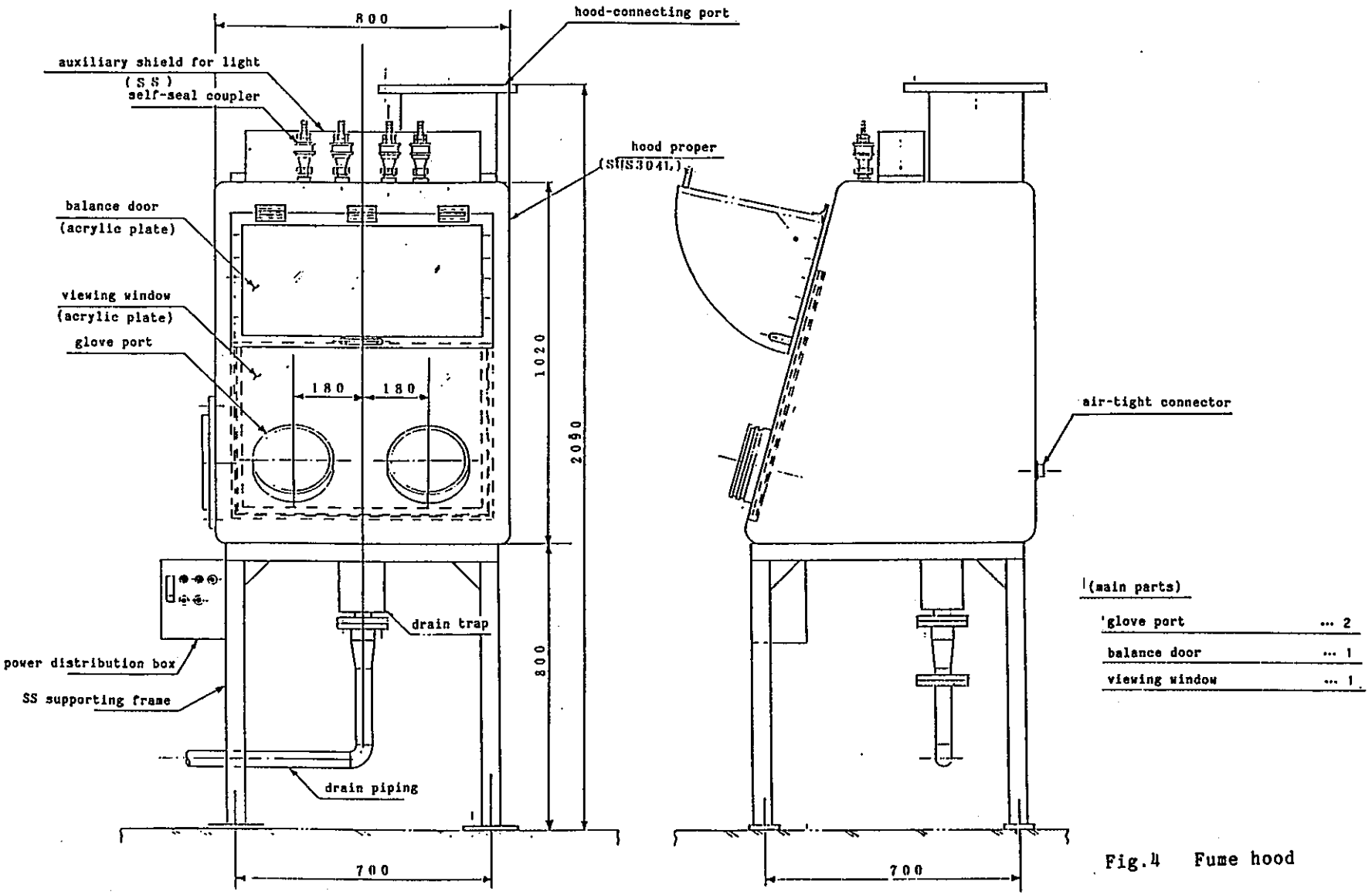


Fig.4 Fume hood

2. Development and Fabrication of Robots for Resin Bead Treatment

2-1. Introduction

The samples of uranium and plutonium contained in feed-accounting solutions (spent-fuel-dissolved solutions) are prepared by the resin bead technique. In addition to the technical problems mentioned in the preceding Section such as (1) great effect of contamination due to the trace-amounts of uranium and plutonium adsorbed by resin beads and (2) difficult handling of resin beads because of their fineness, radiation exposure of operators handling high-level radioactive samples had given another problem.

To solve these problems, a robot for treating resin beads was developed and fabricated (See Fig.s 5 and 6, Photo.s 1 and 2). Automation of resin bead treatment by using the robot can reduce the contamination of samples by the normalization of operations and decrease the exposure of operators.

This robotic resin bead treatment system comprises a mechanism subsystem installed within the shielded glove box and a control subsystem installed outside the shielded glove box and supplying power to the mechanism subsystem. The mechanism subsystem consists of an arm-type robot, a sample turntable, an extraction and mixing turntable, a sealing turntable, a sample-taking tip turntable, an ion-exchange column turntable and a reagent injection device. The control subsystem, on the other hand, consists of a computer, power supply etc.

Using this system, a sample is taken into a resin-bead-containing vial, which is turned to have uranium and plutonium contained in the sample adsorbed by the resin beads. Then the resin beads are transferred to a throw-away ion exchange column to add a reagent for washing. A series of these operations are carried out automatically.

2-2. Place of Installation

The robotic resin bead treatment system was installed within the shielded glove box in the High-level Radioactive Sample Analysis Room (G 105) located in the first floor of the Analysis Laboratory of the PNC/TRP.

2-3. Structure, Dimensions etc. of the System

(1) Mechanism Subsystem within Shielded Glove Box

dimensions : 650 mm wide×480 mm deep×665 mm high

weight : about 40 kg

The mechanism subsystem comprises a sample turntable, an extraction and mixing turntable, a sealing turntable, a sample-taking tip turntable, an ion exchange column turntable and an arm-type robot.

(2) Control Subsystem

dimensions : 570 mm wide ×705 mm deep×1335 mm high

weight : about 120 kg

The control subsystem comprises a computer, a manual control panel and power supply.

(3) Reagent Injection Device

dimensions : 210 mm wide ×240 mm deep×410 mm high

weight : about 6.5 kg

2-4. Operating Sequence

This robotic resin bead treatment system executes sample treatment automatically in accordance with the following operating sequence:

start	• Push the START button to start operation.
↓	
initialization	• Return each unit to the initial positions.
↓	
sample taking	• Attach a tip to the sample taking device.
↓	• Take the sample from a sample bottle, transfer it to a vial, and discard the tip
vial sealing	• Take a plug from the table, and seal the vial with it.
↓	
mixing	• Turn the table for mixing.
↓	
pulling-out of the plug.	• Pull the plug out of the vial, and discard the plug.
↓	
sample transfer	• Attach a new tip to the sample taking device.
↓	• Transfer the sample to a column from the vial, and discard the tip.
reagent injection	• Inject the reagent into the column.
↓	
end	

2-5. Results

This system was installed in the PNC/TRP and used for sample preparation in the 7 th joint experiment, leading to the favorable results. It was confirmed, therefore, that the operations relating to resin bead sampling could be automated, and that thereby the factors for contamination can be removed and the exposure of personnel during working could be reduced.

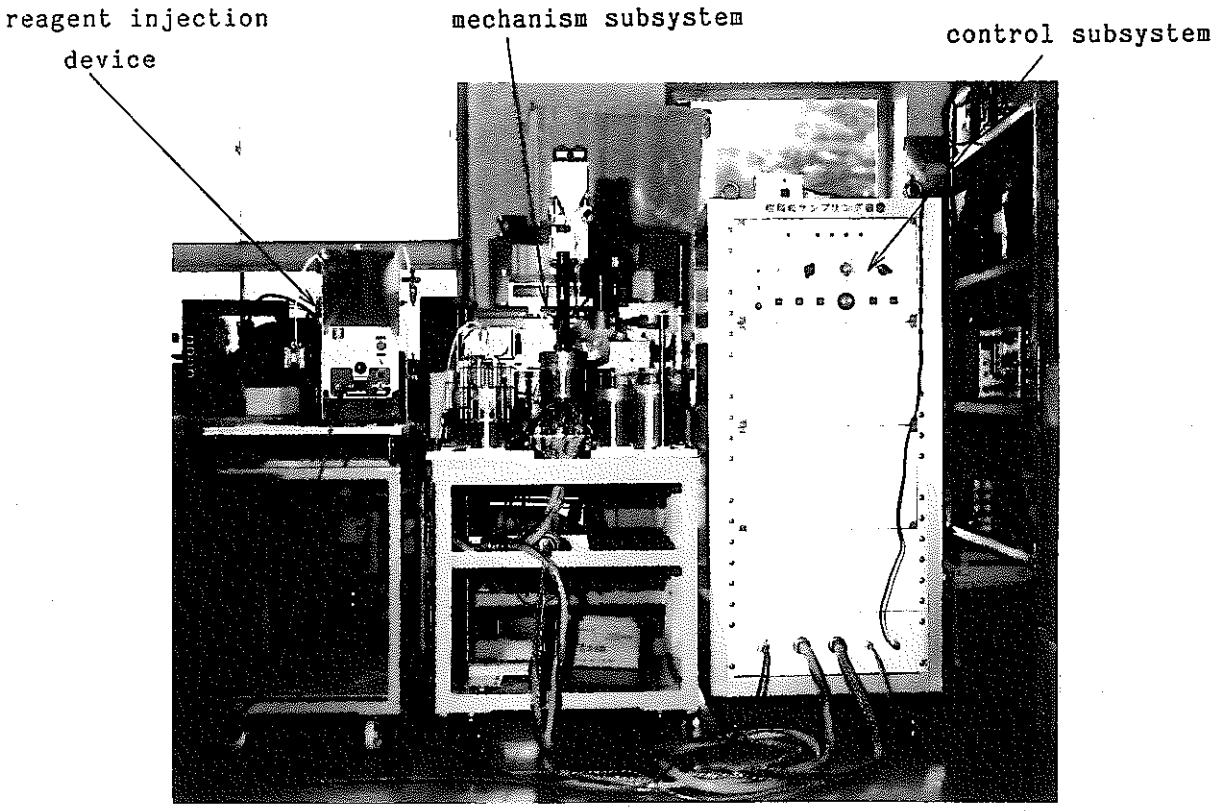


Photo.1 Robotic resin bead treatment system (as a whole)

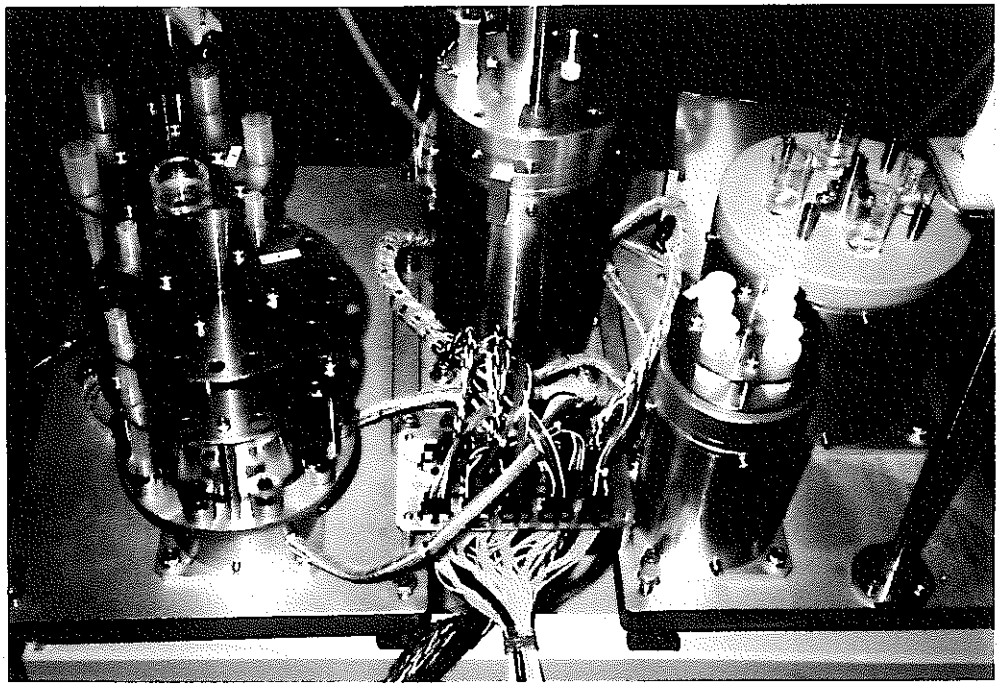


Photo.2 Mechanism Subsystem of robotic resin bead treatment system

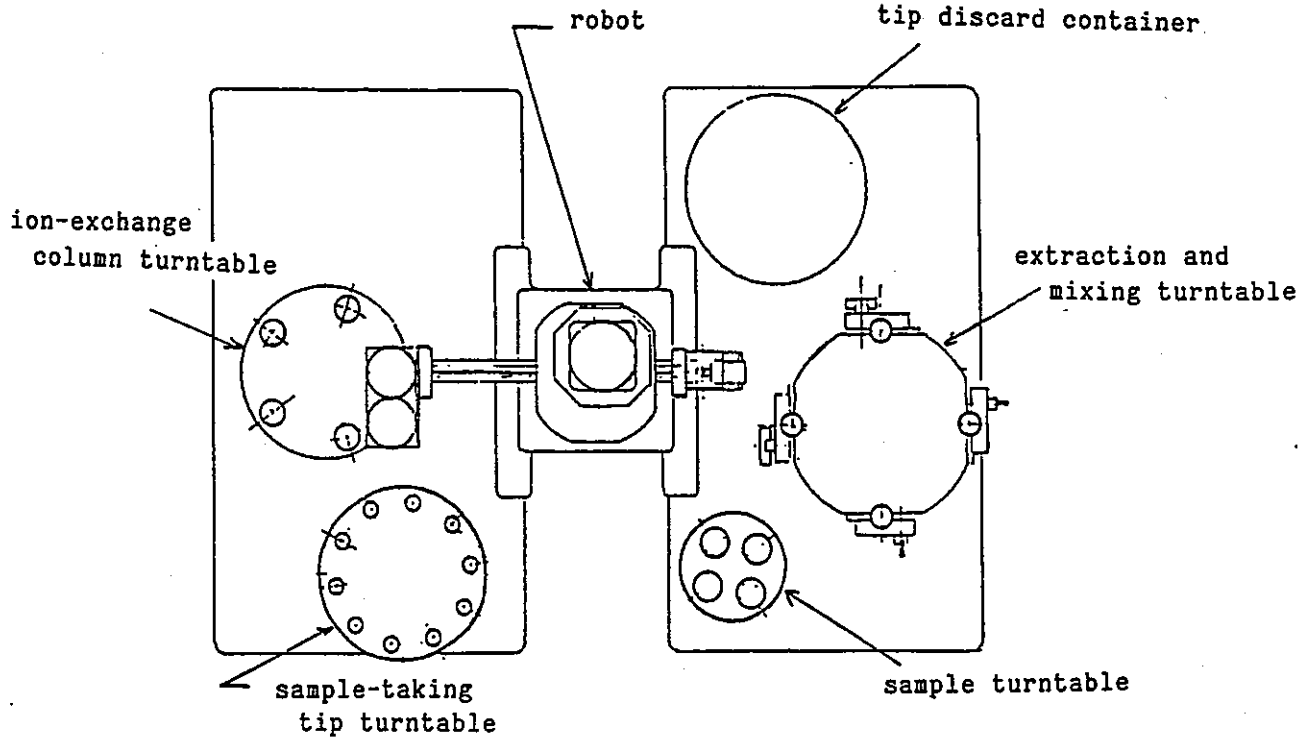


Fig.5 Schematic drawing-1 of robotic resin bead treatment system

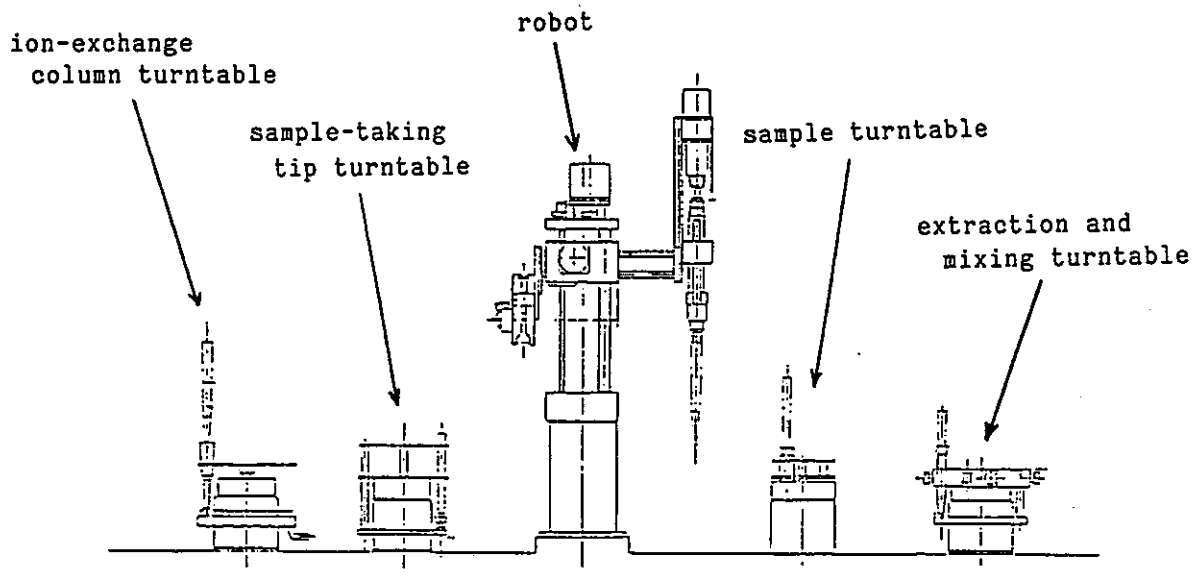


Fig.6 Schematic drawing-2 of robotic resin bead treatment system

Chapter 2 Reports of Joint Experiments on Resin Bead Technique

The reports of the third through seventh joint experiments on the resin bead technique carried out between the PNC and the IAEA-SAL are attached in Chapter 2. The report of the seventh joint experiment, however, was prepared by the PNC based on the comparison of the three partite data (the PNC, IAEA-SAL and NMCC) which had been performed by the IAEA-SAL.

International Atomic Energy Agency

IAEA/RL/106
October 1983

THE THIRD RESIN BEAD EXPERIMENT AT PNC-TRP

Evaluation of Results

Y. Asakura, I Wachi, S. Irinouchi, S. Terakado,
M. Kamata, Y. Kuno, K. Kaminaga, K. Abe
(PNC, Tokai-Mura)

S. Deron, T. Mueller, H. Shimojima
(IAEA, Vienna)

The Third Resin Bead Experiment at PNC-TRP

Evaluation of Results

by

Y. Asakura, I. Wachi, S. Irinouchi, S. Terakado, M. Kamata, Y. Kuno, K. Kaminaga, K. Abe (PNC, Tokai-Mura)

S. Deron, T. Mueller, H. Shimojima (IAEA, Vienna)

1. Introduction

Following the encouraging results of the two experiments carried out under Task J of the TASTEX programme (1), it was decided to run in 1982 a more comprehensive confirmatory test, while awaiting the completion of new installations at PNC-TRP for preparing bead samples and pending initial implementation of the technique.

This third experiment represents a cooperative effort under Task JC4 of the Japanese Technical Support Porgramme to IAEA Safeguards (JASPAS).

2. Outline of the 1982 Experiment

Samples of 9 batches of diluted input solutions were taken, spiked and prepared by PNC-TRP analysts for parallel measurements at the operator's laboratories and at SAL-IAEA. Figure 1 outlines the analytical scheme and Table 1 provides the sampling and dilution data.

The composition of the spike solution provided and characterized by the operator is described in Table 2.

The resin bead samples were prepared on site by PNC-TRP personnel in November 1981 following the procedure applied in the second TASTEX J experiment (1). Each sample contained approximately 1000 beads. They

cont'd

were all shipped in one consignment via air cargo to Vienna and received in SAL-IAEA on 2 June 1982, where they were analyzed in the same month using the ORNL two stage thermal ionization mass spectrometer. PNC-TRP performed their measurements on parallel solution aliquots using a thermal ionization mass spectrometer and the conventional solution loading method.

As in the previous TASTEX-J experiments (1) the objective was to verify that the resin bead measurements can provide element assays agreeing within $\pm$ 0.5% with the operator data.

3. Results and Discussion

The results of the analyses of uranium and plutonium are presented in Tables 3 and 4 respectively. The plutonium results are all referred to the date of the measurements of the PNC operator.

The following observations may be made on these results

(a) Uranium and plutonium isotopic dilution analyses (IDA) by resin bead measurements agree with a precision and accuracy of the order of 0.5% compared with the operator's data.

(b) The $\frac{\text{Pu-240}}{\text{Pu-239}}$, $\frac{\text{Pu-242}}{\text{Pu-239}}$, $\frac{\text{U-235}}{\text{U-238}}$ isotope ratios of the unspiked samples of typical LWR spent fuels may be measured with precisions and accuracies of $\pm$ 0.3, $\pm$ 1.5 and $\pm$ 1% respectively.

(c) Both IDA and the above isotope ratios measurements are limited in precision and accuracy by the mass fractionation effects with resin beads.

cont'd

(d) The $\frac{Pu-238}{Pu-239}$ isotope ratio measurement cannot be made with resin bead loaded with low enriched uranium to better than $\pm$ 10%. This is however sufficient for direct accountancy verification.

(e) The $\frac{U-234}{U-238}$ isotope ratio measurements with resin bead are disturbed by some isobaric or ionization interference.

(f) A bias in the isotopic analysis of the mixed spike requires further investigation (Table 5).

4. Conclusions

The third resin bead experiment at PNC confirms that verifications of uranium and plutonium concentrations of spent fuel solutions may be done by the resin bead technique with a precision and accuracy of the order of 0.5%. It is therefore recommended to start its implementation at PNC-TRP as soon as the new facilities for the preparation of Agency samples are completed at the plant laboratory, i.e. possibly in the second half of 1984.

In the meantime it is suggested to investigate the source of a small bias observed in the isotopic analyses of the plutonium tracer.

Reference

(1) H. Shimojima et al., TASTEX-J Report, IAEA Technical Reports Series No. 213, p. 263 - 176, Vienna (1982).

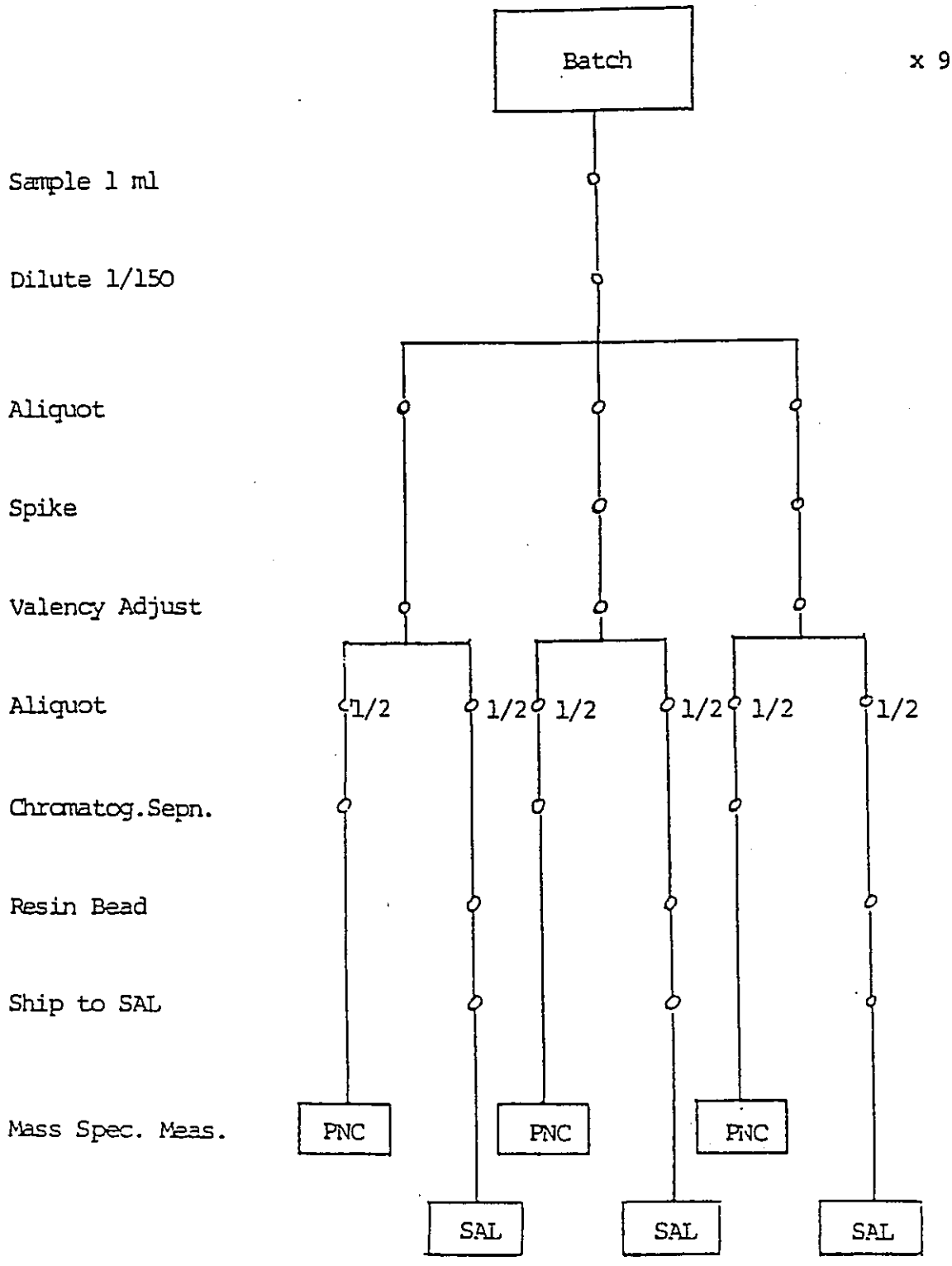


Figure 1 Outline of the third Resin Bead Experiment at PNC-TRP.

Table 1 1982 resin bead experiment at PNC-TRP.

The dilution factors and the spiking data

Batch No.	※1 1st Sampling Volume (mℓ)	※2 Diluted Volume (mℓ)	※3 Dilution Factor	※4 2nd Sampling Volume (mℓ)	Sampling Volume of mix spike (mℓ)
SII - 039	1.0090	149.57	149.23	1.0110	1.0029
SII - 040	1.0092	149.57	149.21	1.0056	1.0033
SII - 041	0.9997	149.57	150.61	1.0232	1.0072
SII - 043	1.0133	149.57	148.61	1.0107	1.0050
SII - 045	1.0006	149.57	150.48	1.0105	1.0061
SII - 047	1.0004	149.57	150.51	1.0081	1.0018
SII - 052	1.0050	149.57	149.83	1.0059	0.9996
SII - 053	1.0085	149.57	149.31	1.0007	1.0061
SII - 055	1.0103	149.57	149.05	1.0132	1.0128

※1 Sampling from dissolver solution.

※2 Volume of 3M HNO3 used to dilute.

※3 $DF = \dfrac{\text{1st Sampling} + \text{Diluted Volume}}{\text{1st Sampling}}$

※4 Sampling from diluted solution of about 150 times.

Table 2 Composition of the mixed spike solution used in the third resin bead experiment at PNC-TRP (Operator's data)

Element	Atom Number in spike solution (atom/ml)
U-233	2.9959×10^{18}
Pu-242	1.2967×10^{16}

Isotope Analysis

		Atom %
U	233	99.508
	234	0.177
	235	0.064
	236	0.015
	238	0.236
Pu	238	0.196
	239	1.669
	240	5.275
	241	0.926
	242	91.791
	244	0.143

Date Meas.:

Table 3 Analyses of Uranium

BATCH	LAB	ISOTOPE RATIOS			ELEMENT CONCENTRATION (g/l)
		(234/238)x100	235/238	(236/238)x100	
SHI-039	PNC	0.0141	0.01209	0.1722	192.51
	SAL	0.0220*	0.01212	0.1719	194.02
	%d	56 *	- 0.21	0.19	- 0.78
SHI-040	PNC	0.0147	0.01208	0.1732	192.01
	SAL	0.0147	0.01200	0.1723	192.65
	%d	0.0	0.71	0.54	- 0.33
SHI-041	PNC	0.0143	0.01211	0.1749	192.02
	SAL	0.0144	0.01207	0.1717	193.29
	%d	- 0.70	0.37	1.80	- 0.66
SHI-043	PNC	0.0148	0.01230	0.1752	180.10
	SAL	0.0138	0.01210	0.1719	181.29
	%d	6.62	1.64	1.87	- 0.66
SHI-045	PNC	0.0149	0.01199	0.1760	188.51
	SAL	0.0147	0.01193	0.1741	188.01
	%d	1.48	0.48	1.09	+ 0.27
SHI-047	PNC	0.0154	0.01217	0.1724	197.23
	SAL	0.0152	0.01219	0.1722	197.99
	%d	1.56	- 0.20	0.11	- 0.38
SHI-52	PNC	0.0137	0.01213	0.1728	191.76
	SAL	0.0142	0.01213	0.1734	193.27
	%d	- 3.58	0.0	-0.36	- 0.79
SHI-053	PNC	0.0131	0.01221	0.1726	194.35
	SAL	0.0148	0.01231	0.1735	196.55
	%d	- 12.7	- 0.84	-0.54	- 1.13
SHI-055	PNC	0.0141	0.01227	0.1741	195.64
	SAL	0.0141	0.01209	0.1722	195.45
	%d	- 0.14	1.48	1.06	+ 0.10
Mean	$\overline{\%d}$	- 0.93	0.38	0.64	- 0.49
Std dev.	SD	5.56	0.81	0.88	0.45
Std error	SE	1.96	0.27	0.29	0.15

* outlier, deleted

Table 4 Analyses of Plutonium

All data referred to PNC dates of measurement (%d = $\frac{PNC-SAL}{PNC}$ x100).

BATCH	DATE OF VALIDITY	LAB	238/239	240/239	241/239	242/239	ELEMENT CONC. (g/l)
SHI-039	81-11-11	PNC	0.00490	0.26129	0.08201	0.02052	0.995
		SAL	0.00511	0.26214	0.08320	0.02111	0.990
		%d	- 4.29	- 0.32	- 1.45	- 2.86	+ 0.50
SHI-040	81-11-12	PNC	0.00484	0.26319	0.08288	0.02123	0.984
		SAL	0.00508	0.26369	0.08304	0.02081	0.977
		%d	- 4.95	- 0.19	- 0.19	1.97	+ 0.71
SHI-041	81-11-13	PNC	0.00494	0.26339	0.08219	0.02075	0.981
		SAL	0.00552	0.26500	0.8303	0.02100	0.982
		%d	- 11.7	- 0.61	- 1.02	- 1.20	- 0.10
SHI-043	81-11-20	PNC	0.00493	0.26163	0.08283	0.02123	0.921
		SAL	0.00538	0.26241	0.08355	0.02130	0.924
		%d	- 9.13	- 0.30	- 0.87	- 0.35	- 0.33
SHI-045	81-11-21	PNC	0.00494	0.26550	0.08451	0.02170	0.993
		SAL	0.00538	0.26615	0.08506	0.02194	1.006
		%d	- 8.91	- 0.244	- 0.65	- 1.12.	- 1.31
SHI-047	81-11-22	PNC	0.00486	0.26220	0.08119	0.02028	1.000
		SAL	0.00503	0.26371	0.08172	0.02044	0.994
		%d	- 3.50	- 0.66	- 0.65	- 0.76	+ 0.60
SHI-052	81-11-27	PNC	0.00489	0.26114	0.08173	0.02044	0.980
		SAL	0.00536	0.26242	0.08339	0.02047	0.981
		%d	- 9.61	- 0.49	- 2.03	- 0.12	- 0.10
SHI-053	81-11-28	PNC	0.00486	0.25865	0.08214	0.02033	1.007
		SAL	0.00620	0.26064	0.08306	0.02070	1.011
		%d	- 27.6	- 0.77	- 1.12	- 1.82	- 0.40
SHI-055	81-11-29	PNC	0.00484	0.26026	0.08133	0.02025	1.006
		SAL	0.00534	0.26205	0.08229	0.02042	1.012
		%d	- 10.3	- 0.687	- 1.18	- 0.86	- 0.60
Mean		$\bar{d}$(%)	± 10.0	± 0.48	± 1.02	± 0.79	- 0.11
Std dev.		SD(%)	± 7.2	± 0.22	± 0.53	± 1.32	0.65
Std error		SE(%)	2.4	0.072	0.17	0.44	0.22

Table 5 Isotopic analyses of the mixed spike

Isotope Ratio	PNC x 100	SAL x 100	%d $\frac{PNC-SAL}{PNC}$ x 100
$\frac{U-234}{U-233}$	0.178	0.181	- 1.7
$\frac{U-235}{U-233}$	0.0643	0.0675	- 5.0
$\frac{U-236}{U-233}$	0.0151	0.0147	+ 2.6
$\frac{U-238}{U-233}$	0.237	0.273	- 15
$\frac{Pu-238}{Pu-242}$	0.214	0.197	7.9
$\frac{Pu-239}{Pu-242}$ (a)	1.818	1.554	14
$\frac{Pu-240}{Pu-242}$	5.747	4.941	14
$\frac{Pu-241}{Pu-242}$	1.009	0.836 (b)	17 (b)
$\frac{Pu-244}{Pu-242}$	0.156	-	
Date Validity		82 06 15	

(a) ORNL value 1.75×10^{-2}

(b) no decay correction

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JASPAS JC-4. Isotopic and Isotope Dilution Analysis of Spent Fuel Solutions by Resin Bead Mass Spectrometry.

Results of the Fourth PNC-IAEA Experiment.

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JASPAS Programme Task JC-4.
Isotopic and Isotope Dilution Analysis of Spent Fuel Solutions by Resin Bead Mass Spectrometry.
Results of the Fourth PNC-IAEA Experiment.

1. Introduction

Nanogramme amounts of uranium and plutonium may be loaded simultaneously on individual beads of anion exchange resin. A single resin bead, mounted on the sample filament of a thermal ionisation mass spectrometer, suffices to perform sequentially a complete isotopic analysis of plutonium and uranium. The method known as the Resin Bead Mass Spectrometry Technique, was proposed by Carter and al (1) for the isotopic and isotope dilution analysis of spent fuel solutions. The implementation of this technique for safeguards verifications of the input to spent fuel reprocessing plants is expected to facilitate the shipment of the necessary samples.

The Resin Bead Technique (RBT) was submitted to two field tests in cooperation with the Reprocessing Plant of the "Gesellschaft zur Wiederaufarbeitung von Kernbrennelementen", the "Kernforschungszentrum Karlsruhe" (KfK), the Oak Ridge National Laboratory (ORNL) and the Safeguards Analytical Laboratory of the Agency (SAL), under the Joint Programme of the Federal Republic of Germany and the IAEA for the Development of Safeguards, and the Technical Support Programme of the USA to Agency Safeguards. The results of the isotopic analyses in these tests were in good agreement with the results of conventional mass spectrometric measurements, but the isotope dilution analyses indicated that neither the reduction with hydroxylamine (2) nor the oxydation with perchloric acid (3) were fully successful in achieving the isotopic equilibrium of plutonium under inspection like conditions.

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The RBT was also the subject of the Task J of the TASTEX programme which involved the cooperation of the Tokai-Mura Reprocessing Plant of the Power Reactor and Nuclear Fuel Development Corporation, Tokai Reprocessing Plant (PNC-TRP), ORNL and SAL. Both exercises performed under this Task gave good assays of plutonium, using divalent iron (Fe(II) and nitrite to adjust the valency and the isotopic equilibrium of plutonium (4). Risks of contamination of the samples with uranium were detected in the first exercise, but were apparently eliminated in the second one after increasing the size of the aliquot of solution taken to prepare the resin beads.

PNC-TRP and SAL pursue now their cooperation on the testing of the RBT under Task JC-4 of the Japanese Support Programme to Agency Safeguards (JASPAS). The first activity under this new task was a third exchange of spent fuel samples in 1981-1982 between PNC-TRP and SAL. Its results (5) confirmed the observations of the Tastex exercises, that the RBT is capable of achieving relative precisions and accuracies of 0.5% in uranium and plutonium isotope dilution assays of safeguarded spent fuel solutions.

PNC-TRP undertook then to design and install a chain of three glove boxes (Figure 1) intended for the implementation of the preparation of inspection samples in resin bead form. A fourth PNC-IAEA Resin Bead Experiment was also conducted to accumulate practical experience on the method, while awaiting the completion of the new glove box installations.

The purpose of this paper is to report on the results of the fourth exercise and to examine the experience acquired at this time in the Task JC-4 of JASPAS.

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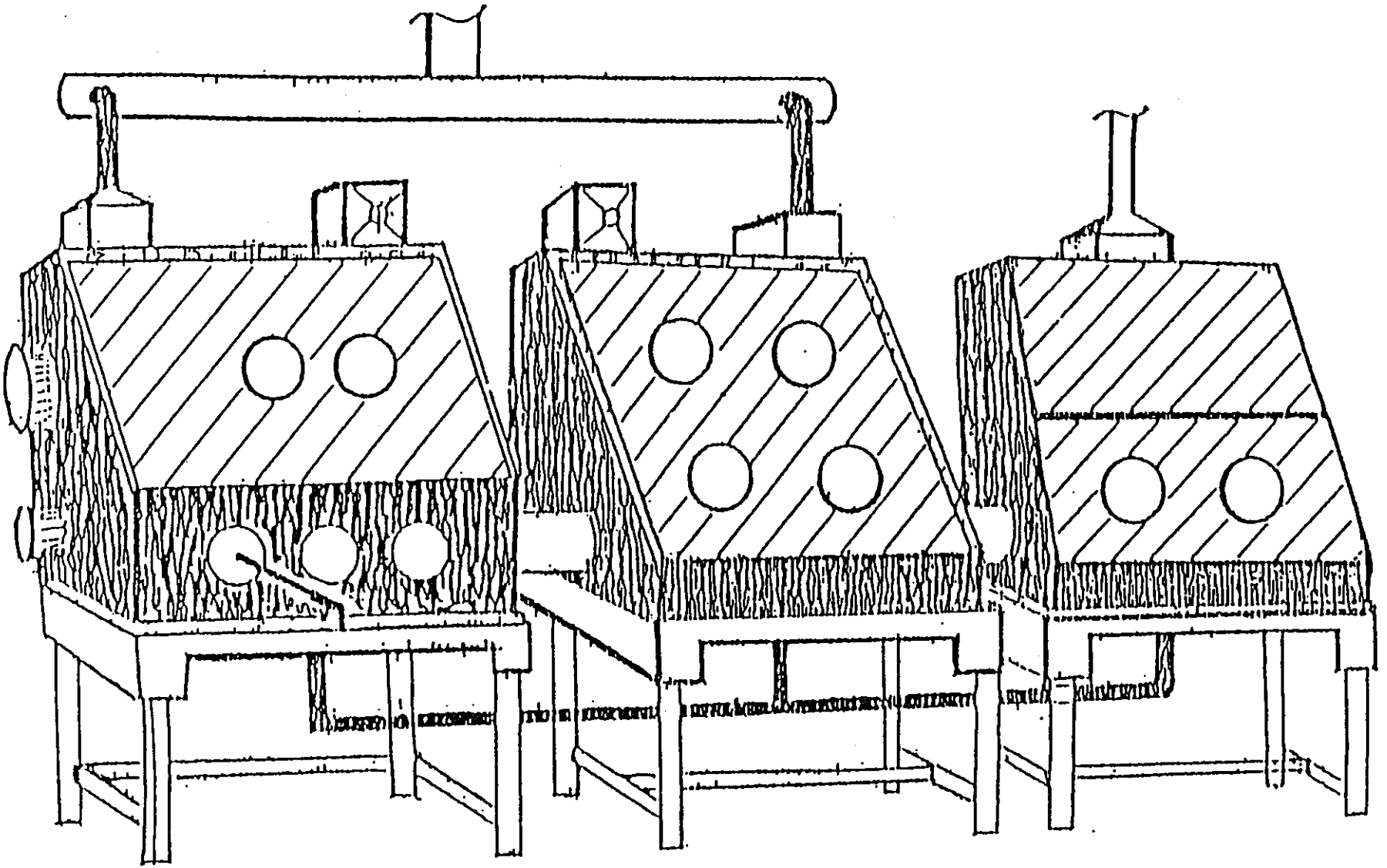
Figure 1: Schematic View of Special Glove Boxes
for future preparation of resin bead samples at PNC-TRP



2. Design of the Experiment and Preparation of the Samples

The PNC-TRP laboratory sampled in October 1982 ten batches of the current input solutions. Each sample was diluted with calibrated volumetric ware; an aliquot of the diluted solution was carefully measured with a calibrated pipet and mixed with a measured volume of a standardized solution of U-233 and Pu-242 isotopic tracers. PNC-TRP used the spiked mixture to prepare about 1000 resin beads according to the Batch Procedure, already adopted in the second and third experiments (4,5). A separate aliquot of the diluted spent fuel solution was taken for isotopic analyses and loaded on resin beads also at the plant according to the Batch Procedure.

In addition, PNC-TRP prepared also a resin bead sample of the mixed tracer solution for its isotopic analysis at SAL.

Figure 2 summarizes the preparation of the resin bead samples for the experiment.

The resin bead samples were shipped from Tokai-Mura in a Type A package by air freight and were received in SAL in April 1983.

3. Results and Discussion

Figure 3 outlines the plan of the replicate measurements performed on each batch of spent fuel solution.

Annex 1 gives the data of PNC-TRP regarding the composition of the mixed tracer solution, and Annex 2 the data of PNC-TRP regarding the dilution and the spiking of the samples.

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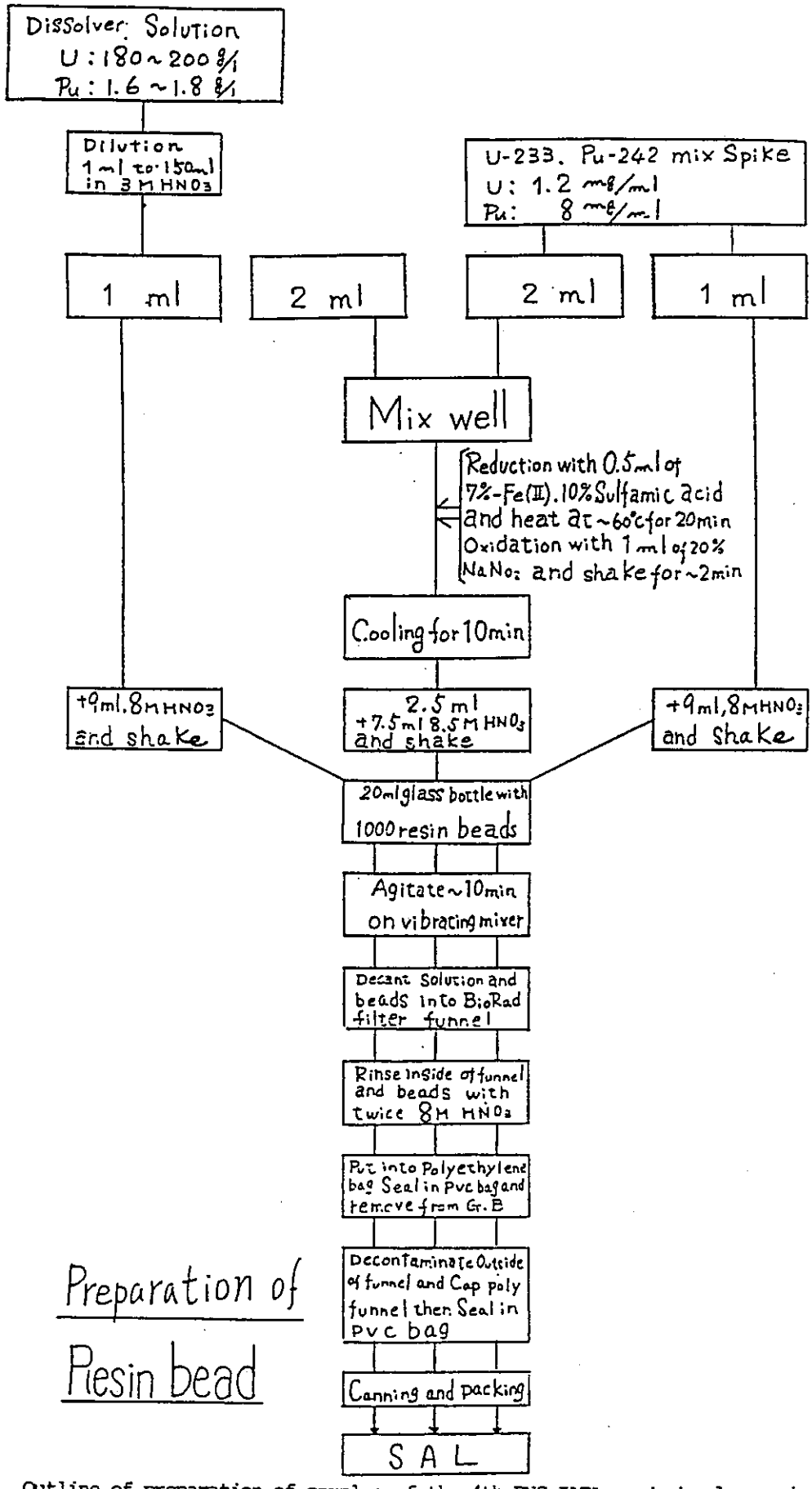

Figure 2 Outline of preparation of samples of the 4th PNC-IAEA resin bead experiment

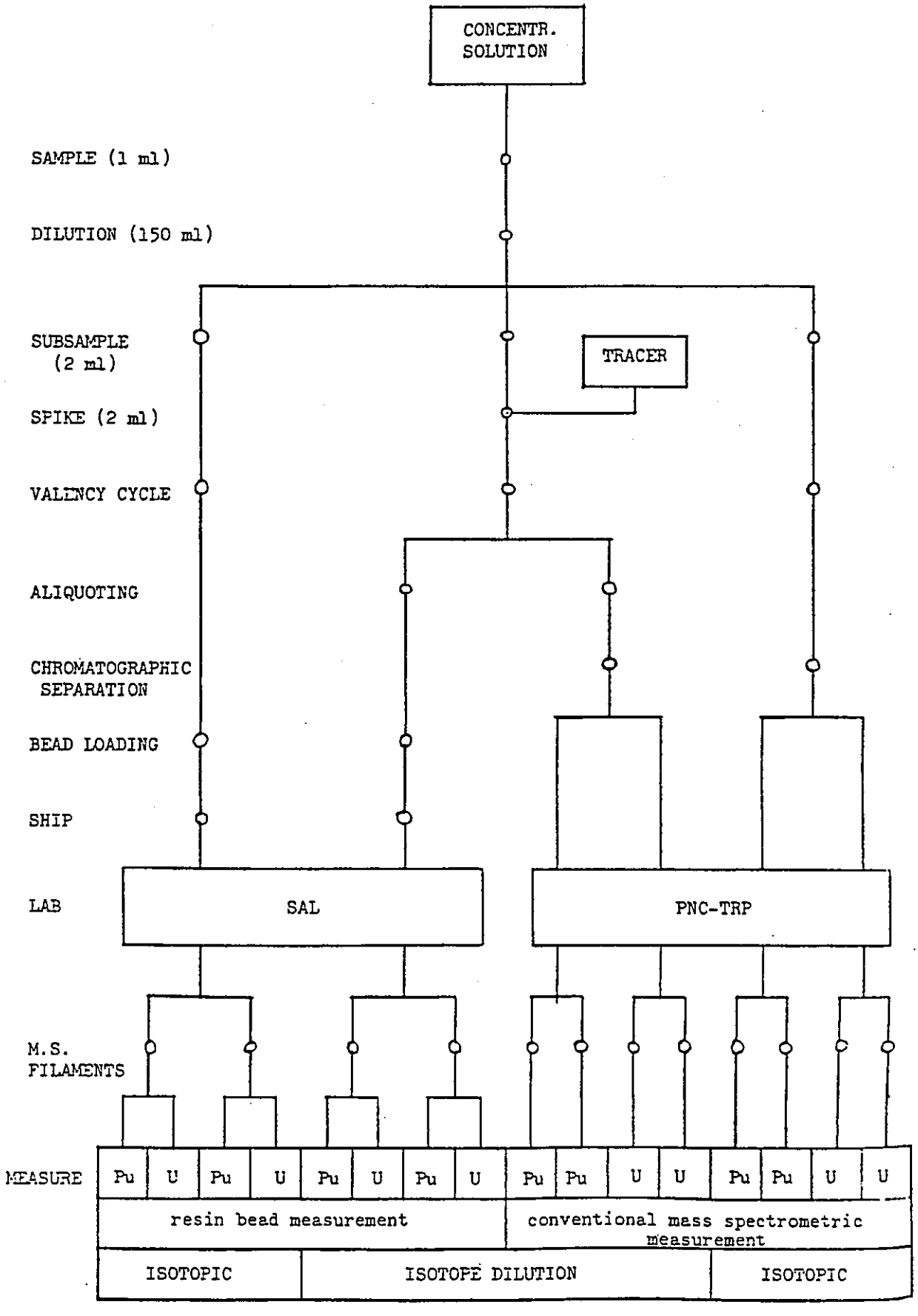

Figure 3: Outline of Measurement Plan

Annexes 3 and 4 present the results of the analyses of the spent fuel samples respectively at PNC-TRP and SAL.

PNC-TRP performed its measurements with conventional solution drop loadings.

SAL made its resin bead measurements with its ORNL-made 2-stage thermal ionization mass spectrometer (6). The measurements were done in three periods, namely June 1983, August 1983 and January 1984. In June and August 1983 the beads were measured as received, while in January 1984 they were measured after stripping the americium by soaking the beads 24 hours in 8M HNO_3 acid.

3.1. Calibration of the resin bead measurements

Calibration was based on the isotopic analyses of resin beads loaded simultaneously with NBS-Pu-947 and NBS-U-010 reference materials. In all three periods of measurements the mass discrimination effects appeared to be abnormally high.

The mass discrimination factors calculated from the analyses of the resin bead reference materials are reported in Table 1, which gives also the means of the results of the isotopic assays, their standard deviations, and coefficients of variation, and the apparent relative biases of the means.

cont'd

Table 1 FOURTH PNC-IAEA RESIN BEAD EXPERIMENT
RESULTS OF MASS SPECTROMETRY CALIBRATIONS

R.M.	ISOTOPE RATIO	NBS Value (83 08 10)	Measured Value (83 08 10)			Relative Diff.	Discrimination Factor
			Mean	STD.DEV.	C.V. (in %)		
NBS-Pu-947	$\frac{238}{239}$	0.00356	0.00344	0.00063	18	-3.4	0.9869
	$\frac{240}{239}$	0.24138	0.24136	0.00067	0.28	-0.01	1.0131
	$\frac{241}{239}$	0.03389	0.0357	0.0025	7.2	+5.3	1.0224
	$\frac{242}{239}$	0.01559	0.01559	0.00025	1.6	0	1.0315
NBS-U-010	$\frac{234}{238}$	0.0000547	0.0000559	0.0000015	2.6	-2.2	0.9562
	$\frac{235}{238}$	0.01014	0.010150	0.000017	0.17	+0.1	0.9672
	$\frac{236}{238}$	0.0000688	0.0000722	0.0000021	3.0	+4.9	0.9781

3.2. Resin Bead Isotopic Analyses of the Mixed Tracer

The resin beads loaded with the mixed tracer were measured as received.

The results of the isotope ratio and abundance measurements for the tracer are compared in Tables 2 and 3 with the PNC data. A similar comparison is presented in Table 4 for the isotopic abundances of the samples.

The plutonium results are in good agreement, except for the Pu-241 isotope where most resin bead measurements were biased by americium interference.

The results of the resin bead measurements of the uranium isotope ratios are all significantly lower than the PNC data. These differences can result from a blank in the resin bead measurements equivalent to a contamination by 0.0374×10^{18} atoms, i.e. 14.8 µg of natural uranium per ml of tracer.

This blank amounts thus to 1.2% of the total uranium in the tracer.

cont'd

Table 2 FOURTH PNC-IAEA RESIN BEAD EXPERIMENT
RESULTS OF ISOTOPE RATIOS OF THE TRACER

ELEMENT	ISOTOPE RATIO	PNC value (82 09 30)	SAL Result (82-09-30)			Relative Diff.* (in %)
			Mean	STD.DEV.	C.V. (in %)	
PLUTONIUM	$\frac{238}{239}$	0.04395	0.0441	0.0016	3.6	0.34
	$\frac{240}{239}$	1.6945	1.698	0.0092	0.54	0.21
	$\frac{241}{239}$	0.9298	0.974	0.042	4.3	4.7
	$\frac{242}{239}$	53.44	53.29	0.50	0.94	-0.28
	$\frac{244}{239}$	-	0.00145	0.00008	5.5	-
URANIUM	$\frac{233}{238}$	490.6	66.84	13.5	20	-86
	$\frac{234}{238}$	0.9248	0.125	0.025	20	-86
	$\frac{235}{238}$	0.3144	0.0658	0.0018	2.7	-79
	$\frac{236}{238}$	0.0759	0.0109	0.0016	15	-86

* $\frac{\text{SAL-PNC}}{\text{PNC}} \times 100$

Table 3 FOURTH PNC-IAEA RESIN BEAD EXPERIMENT
RESULTS OF ISOTOPIC ABUNDANCES OF THE TRACER
(in atom %)

ELEMENT	ISOTOPE	PNC value (82 09 20)	SAL value (82 09 20)	Relative Diff. (in %)
PLUTONIUM	Pu-238	0.0770	0.0774	0.52
	Pu-239	1.7510	1.754	0.17
	Pu-240	2.9671	2.979	0.40
	Pu-241	1.6281	1.708	4.9
	Pu-242	93.574	93.479	0.10
	Pu-244	(0.0025)(1)	0.0025	-
URANIUM	U-233	99.530	98.234	-1.30
	U-234	0.1876	0.1837	-2.1
	U-235	0.0638	0.0967	51.6
	U-236	0.0154	0.0160	3.9
	U-238	0.2029	1.470	624.0

(1) Calculated using the $\frac{\text{Pu-244}}{\text{Pu-239}}$ ratio measured by SAL.

3.3. Reproducibility of resin bead measurements

The reproducibility of replicate resin bead measurements (Table 4) was generally acceptable. Difficulties were however experienced in measuring the Pu-241/Pu-239 isotope ratio on the samples received, because of Am-241 interfrence. Better results were generally obtained in January 1984 after washing the beads (Table 5). But the latter treatment strips also part of the uranium, which was then more difficult to analyze. This, and possible variations in the high mass discrimination factor of - 5.5% explain why the coefficient of variation of the measurements of the U-233/U-238 isotope ratio was as high as 1%.

3.4. Comparison of isotope ratio measurements

The plutonium isotope ratio measurements are in good agreement (Table 6) except for the following cases:

(a) the resin bead measurements of the Pu-238/Pu-239 isotope ratios, although they are reproducible (Table 4), are on the average 23% lower than the conventional measurements;

(b) for the batch 60, there is a 2% difference on the Pu-240/Pu-239 ratio, and 3.5% on the Pu-242/Pu-239 ratio between the results of the two methods.

cont'd

Table 4 FOURTH PNC-IAEA RESIN BEAD EXPERIMENT
PRECISION OF RESIN BEAD MEASUREMENTS

ELEMENT	ISOTOPE RATIO	AVERAGE ISOTOPE RATIO	AVERAGE COEFF OF VARIATION in %	DEGREES OF FEEDOM
PLUTONIUM	$\frac{238}{239}$	0.0242	1.6	12
	$\frac{240}{239}$	0.3790	0.33	13
	$\frac{242}{239}$	0.0695	1.06	13
URANIUM	$\frac{234}{238}$	0.00020	8.9	12
	$\frac{235}{238}$	0.01098	0.86	12
	$\frac{236}{238}$	0.00372	0.76	11
SPIKED PLUTONIUM	$\frac{242}{239}$	0.9814	0.58	24
SPIKED URANIUM	$\frac{233}{238}$	0.9369	1.05	22

Table 5 FOURTH PNC-IAEA RESIN BEAD EXPERIMENT
RESULTS OF Pu-241/Pu-239 MEASUREMENTS
(data referred to the date of the PNC measurement)

Batch	Date of Validity	PNC	SAL (1)	SAL (2)
50	82-10-13	0.1890	0.1699 (3)	0.2035 (3)
51	82-10-14	0.1885	0.1889 (4)	0.1899 (3)
54	82-10-17	0.1875	0.1899 (4)	0.1944 (3)
55	82-10-18	0.1808	0.1809 (3)	0.1825 (4)
58	82-10-22	0.1404	0.1426 (4)	0.1427 (3)
59	82-10-24	0.1668	0.1636 (4)	0.1807 (3)
60	82-10-25	0.1509	0.1530 (4)	0.1592 (3)
61	82-10-26	0.1599	0.1605 (4)	0.1945 (3)
63	82-10-28	0.1824	0.1818 (4)	0.1936 (3)
64	82-10-29	0.1895	0.1890 (4)	0.2109 (3)
Mean relative diff's		% $\bar{d}$	0.28	6.76
Standard deviation of relative diff.		SD	$\pm$ 1.03	$\pm$ 6.26
Number of measurements		(n)	(10)	(10)

(1) Best result with minimum evidence of Am-241 interference

(2) Result with significant Am-241 interference

(3) Measurement on bead as received

(4) Measurement after washing

(5) Relative diff., $d\% = \frac{SAL-PNC}{PNC} \times 100$

Table 6 FOURTH PNC-IAEA RESIN BEAD EXPERIMENT
RESULTS OF MEASUREMENTS OF PLUTONIUM ISOTOPE RATIOS *)

BATCH	LAB	$\frac{238}{239}$	$\frac{240}{239}$	$\frac{241}{239}$	$\frac{242}{239}$	S $\frac{242}{239}$ (1)
50	P	0.0250	0.3843	0.1890	0.0679	1.0184
	S	0.0202	0.3857	0.1899	0.0683	1.0294
51	P	0.0221	0.3829	0.1885	0.0675	1.0052
	S	0.0203	0.3850	0.1889	0.0679	1.0292
54	P	0.0240	0.3817	0.1875	0.0666	1.0070
	S	0.0205	0.3849	0.1899	0.0683	0.7255(5)
55	P	0.0361	0.3934	0.1808	0.0801	1.0279
	S	0.0310	0.3955	0.1809	0.0794	1.0236
58	P	0.0249	0.3304	0.1404	0.0523	0.9870
	S	0.0214	0.3295	0.1426	0.0529	0.9929
59	P	0.0430	0.3933	0.1668	0.0783	1.0495
	S	0.0284	0.3893	0.1636	0.0765	1.0469
60	P	0.0368	0.3576	0.1509	0.0623	1.0280
	S	0.0239	0.3650	0.1530	0.0645	1.0222
61	P	0.0269	0.3820	0.1599	0.0710	0.9897
	S	0.0263	0.3837	0.1605	0.0713	0.9892
63	P	0.0413	0.3806	0.1824	0.0692	0.9933
	S	0.0228	0.3804	0.1818	0.0699	0.9879
64	P	0.0470	0.3911	0.1895	0.0770	0.9664
	S	0.0275	0.3910	0.1890	0.0763	0.9673
(2)	$\bar{d}$	- 23	0.34	0.28	0.58	0.26
(3)	sd	± 15	± 0.80	± 1.03	± 1.69	± 0.97
(4)	(n)	(10)	(10)	(10)	(10)	(9)

*) valid for the date of the PNC measurement.

(1) Results of measurements of spiked samples

(2) Mean relative diff., $\bar{d} = \frac{SAL-PNC}{PNC} \times 100$

(3) Standard deviation of relative diff.

(4) Number of diff. data used in the calculations

(5) Value rejected in the calculation.

(c) With the spiked sample of batch 54, the resin bead measurement of the Pu-242/Pu-239 ratio is 28% lower than the conventional measurement; a contamination of this sample with plutonium is suspected.

The uranium isotope ratio measurements are compared in Table 7. The following remarks may be made:

(i) There is a small isobaric interference in the resin bead measurement of the U-234/U-238 ratio

(j) The negative biases of the resin bead measurements of the U-235/U-238 and U-233/U-238 are a consequence of the small blank of natural uranium detected in the isotopic analysis of the tracer (see section 3.2).

3.5. Comparison of isotopic and isotope dilution analytical results

Tables 8 and 10 give the results of the calculations of the isotopic abundances and concentrations of plutonium and uranium in the 10 batches of spent fuel solutions.

The isotopic abundances are directly derived from the isotope ratio measurements reported in Tables 7 and 8, without blank corrections.

But a blank correction is included in the calculations of the element concentrations as well as in the calculations of the concentrations of the isotope Pu-239 reported in Table 9. To perform this correction, the resin bead results of SAL were evaluated using the mean isotopic composition of the tracer loaded on resin beads (Table 2), while PNC-TRP calculated the results of its isotope

cont'd

Table 7 FOURTH PNC-IAEA RESIN BEAD EXPERIMENT

RESULTS OF MEASUREMENTS OF URANIUM ISOTOPE RATIOS

BATCH	LAB	$\frac{234}{238}$ x 100	$\frac{235}{238}$ x 100	$\frac{236}{238}$ x 100	S $\frac{233}{238}$ (1)
50	P	0.0154	0.9114	0.3145	0.9300
	S	0.0195	0.899	0.3125	0.9070
51	P	0.0152	0.9150	0.3145	0.9336
	S	0.0195	0.9105	0.315	0.9063
54	P	0.0153	0.9156	0.3136	0.9156
	S	0.0185	0.902	0.312	0.9010
55	P	0.0190	1.0906	0.4332	0.9882
	S	0.0235	1.0885	0.4355	0.9794
58	P	0.0212	1.4946	0.3847	0.9418
	S	0.025	1.494	0.387	0.9267
59	P	0.0192	1.1260	0.3940	1.0042
	S	0.029	1.126	0.396	0.9964
60	P	0.0203	1.3035	0.4001	0.9881
	S	0.025	1.312	0.403	0.9834
61	P	0.0191	1.1360	0.3901	0.9609
	S	0.023	1.146	0.394	0.9308
63	P	0.0177	1.044	0.3421	0.9223
	S	0.0215	1.021	0.352	0.9197
64	P	0.0201	1.0814	0.4072	0.9281
	S	0.0275	1.0835	0.410	0.9179
(2)	% $\bar{d}$	+ 27	- 0.40	+ 0.60	- 1.53
(3)	SD	$\pm$ 10	$\pm$ 0.99	$\pm$ 0.97	$\pm$ 1.01
(4)	(n)	(10)	(10)	(10)	(10)

(1) Results of measurements of spiked samples

(2) Mean relative diff., $\bar{d} = \frac{SAL-PNC}{PNC} \times 100$

(3) Standard deviation of relative diff.

(4) Number of diff. data used in the calculations.

dilution analyses with its own tracer data (Annex 1). But the concentrations of U-233 and Pu-242 isotopes in the tracer defined by PNC-TRP (Annex 1) were adopted in making both sets of calculations.

The following observations are relevant:

(a) The low values of Pu-238/Pu-239 obtained on resin beads (Table 6) cause a negative bias (with respect to PNC) of the Pu-238 isotopic abundance, but also a negative bias in the results of the plutonium concentration, and a positive bias in all other isotopic results (Table 8).

(b) The results of the Pu-239 concentrations (Table 9) do not suffer from this effect: the mean relative difference is less than 0.3% between the two methods.

(c) After blank correction there was no statistical significant difference between the uranium concentration results of the two methods: their mean relative difference is less than 0.2%.

(d) The standard deviations of the relative differences of the concentration results are however larger than desirable: 0.9% for plutonium and uranium, 1.0% for Pu-239. This reflects probably the difficulty to reproduce the mass discrimination effects, which were about 0.3 - 0.5% per mass larger than usual in the present exercise of resin bead measurements.

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Table 8 FOURTH PNC-IAEA RESIN BEAD EXPERIMENT

RESULTS OF ISOTOPIC AND ISOTOPE DILUTION ANALYSES OF PLUTONIUM

(data referred to the date of PNC-TRP measurement)

BATCH	LAB	Pu-238 in wgt%	Pu-239 in wgt%	Pu-240 in wgt%	Pu-241 in wgt%	Pu-242 in wgt%	Pu in g/l
50	P	1.490	59.878	23.106	11.412	4.114	1.586
	S	1.206	59.949	23.219	11.480	4.146	1.566
51	P	1.322	60.064	23.094	11.417	4.103	1.576
	S	1.213	60.022	23.205	11.433	4.127	1.538
54	P	1.434	60.111	23.040	11.363	4.052	1.529
	S	1.224	59.967	23.178	11.483	4.147	2.204 (4)
55	P	2.122	59.019	23.317	10.758	4.784	1.594
	S	1.826	59.142	23.489	10.789	4.755	1.596
58	P	1.600	64.468	21.387	9.130	3.414	1.452
	S	1.375	64.535	21.353	9.280	3.457	1.442
59	P	2.537	59.340	23.438	9.980	4.706	1.535
	S	1.702	60.181	23.527	9.928	4.662	1.515
60	P	2.274	62.072	22.289	9.447	3.918	1.465
	S	1.478	62.115	22.767	9.583	4.057	1.439
61	P	1.627	60.846	23.344	9.810	4.373	1.567
	S	1.592	60.770	23.415	9.835	4.387	1.571
63	P	2.452	59.618	22.788	10.965	4.176	1.594
	S	1.369	60.284	23.028	11.052	4.267	1.587
64	P	2.740	58.528	22.983	11.184	4.565	1.678
	S	1.622	59.246	23.262	11.291	4.577	1.655
(1)	$\%\bar{d}$	-22.5	0.38	0.72	0.66	0.97	-0.98
(2)	SD	$\pm$14.5	$\pm$0.62	$\pm$0.63	$\pm$0.65	$\pm$1.39	$\pm$0.87
(3)	(n)	(10)	(10)	(10)	(10)	(10)	(9)

(1) Mean of relative diff., $d = \frac{SAL-PNC}{PNC} \times 100$

(2) Standard deviation of differences

(3) Number of diff. data used in calculations

(4) Value deleted in the calculations.

Table 9 FOURTH PNC-IAEA RESIN BEAD EXPERIMENT

COMPARISON OF THE RESULTS OF THE ISOTOPE DILUTION DETERMINATION OF THE Pu-239 CONCENTRATION

(data referred to the date of the PNC measurement)

BATCH	P in g/l	S in g/l	%d
50	0.9494	0.9388	- 1.12
51	0.9468	0.9231	- 2.50
54	0.9335	1.3217	+44.53 (1)
55	0.9405	0.9439	0.36
58	0.9360	0.9306	- 0.58
59	0.9112	0.9119	0.08
60	0.9095	0.9171	+ 0.84
61	0.9535	0.9547	0.13
63	0.9504	0.9567	0.66
64	0.9822	0.9805	- 0.17
Mean relative diff.		% $\bar{d}$	- 0.26
Standard deviation		SD	$\pm$ 1.04
(Number of values)		(n)	(9)

(1) Value deleted in the calculation of the mean and standard deviation.

Table 10 FOURTH PNC-IAEA RESIN BEAD EXPERIMENT
RESULTS OF ISOTOPIC AND ISOTOPE DILUTION ANALYSES OF URANIUM
(data referred to the date of PNC-TRP measurement)

BATCH	LAB	U-234 in wgt%	U-235 in wgt%	U-236 in wgt%	U-238 in wgt%	U in g/l
50	P	0.0150	0.8890	0.3081	98.788	190.66
	S	0.0189	0.877	0.306	98.798	193.1
51	P	0.0148	0.8925	0.3081	98.785	186.79
	S	0.0189	0.888	0.309	98.784	190.1
54	P	0.0149	0.8931	0.3072	98.785	185.37
	S	0.0180	0.880	0.306	98.796	186.1
55	P	0.0184	1.0607	0.4231	98.498	177.77
	S	0.0229	1.059	0.425	98.493	177.1
58	P	0.0205	1.4486	0.3744	98.157	183.58
	S	0.0241	1.448	0.377	98.151	184.3
59	P	0.0186	1.0951	0.3848	98.501	173.74
	S	0.0281	1.095	0.387	98.492	172.8
60	P	0.0196	1.2655	0.3901	98.325	175.48
	S	0.0242	1.274	0.393	98.309	174.2
61	P	0.0185	1.1048	0.3810	98.496	181.88
	S	0.0222	1.114	0.385	98.479	183.1
63	P	0.0172	1.0167	0.3346	98.632	187.29
	S	0.0209	0.994	0.344	98.641	185.5
64	P	0.0195	1.0521	0.3978	98.531	185.22
	S	0.0266	1.054	0.401	98.519	185.0
(1)	$\%\bar{d}$	27	-0.40	0.62	-0.004	0.17
(2)	SD	$\pm$10	$\pm$0.98	$\pm$0.96	$\pm$0.011	$\pm$0.89
(3)	(n)	(10)	(10)	(10)	(10)	(10)

(1) Mean of relative diff., $\bar{d} = \frac{\text{SAL-PNC}}{\text{PNC}} \times 100$

(2) Standard deviation of differences

(3) Number of diff. data used in the calculation.

4. Conclusions

Table 11 summarizes the results obtained in the last three intercomparisons carried out between PNC-TRP and IAEA-SAL under the task JC-4 of the JASPAS programme.

Focussing on the results of the determinations of the uranium and plutonium concentrations, the three experiments confirm that resin bead measurements can in the present state of the practice agree on the average to $\pm$ 0.5% with operator data, with standard deviations of 0.5% or less for the systematic errors. This performance is within the goals which have been set as "1983 target values" for the accuracy of safeguards verification measurements (7). The average precision of these measurements is however not as good as desirable: their average standard deviations are 0.7 - 0.9% compared to "target values" of 0.5%. Actually a significant deterioration of the precision is evident in the fourth intercomparison, which is the principal topic of the present report.

The experience accumulated at this time in the task JC-4 allows to point out the factors which limit the performance of the resin bead technique at this time and which need to be properly controlled in its application.

The major source of systematic errors in the isotopic and isotope dilution analyses lies in the potential errors of the correction of the mass discrimination effects. Their accurate correction requires calibration of the mass spectrometer with resin beads loaded with isotopic reference materials of uranium and plutonium, respectively. The calibration plan must include the measurements of resin beads loaded with 1 : 1 certified mixtures of U-233 with U-238 isotopes, and Pu-242 or Pu-244 with Pu-239 isotopes. New Brunswick Laboratory (NBL) provides a 1 : 1 : 1 mixture of the U-233, U-235, U-238 isotopes, which is ideal for preparing resin beads for the calibration of uranium analyses: its NBL-117 CRM (8).

cont'd

Table 11 SUMMARY OF THE RESULTS OF 3 PNC-IAEA RESIN BEAD EXPERIMENTS
MEAN RELATIVE DIFFERENCES AND STANDARD DEVIATIONS

SAMPLE	MEASUREMENT	EXPERIMENT			OVERALL MEAN DIFFERENCE AND STD. DEV.
		No. 2	No. 3	No. 4	
UNSPIKED	U-234/U-238	- 7.6 (1)	+ 0.93 - 5.5 (8)	+ 27 - 10 (10)	+ 15 - 15 (19)
	U-235/U-238	- 0.35 (1)	+ 0.38 - 0.81 (9)	+ 0.40 - 0.99 (10)	+ 0.39 - 0.85 (20)
	U-236/U-238	- 1.2 (1)	+ 0.64 - 0.88 (9)	+ 0.60 - 0.97 (10)	+ 0.05 - 1.10 (20)
	Pu-238/Pu-239	- 7.3 (1)	+ 10 - 7.2 (9)	+ 23 - 15 (10)	+ 7.2 - 20 (20)
	Pu-240/Pu-239	- 0.10 (1)	+ 0.47 - 0.22 (9)	+ 0.34 - 0.80 (10)	+ 0.38 - 0.59 (20)
	Pu-241/Pu-239	+ 0.97 (1)	+ 1.02 - 0.53 (9)	+ 0.28 - 1.03 (10)	+ 0.65 - 0.87 (20)
	Pu-242/Pu-239	+ 0.12 (1)	+ 0.79 - 1.32 (9)	+ 0.58 - 1.69 (10)	+ 0.65 - 1.45 (20)
SPIKED	U-233/U-238	+ 0.02 - 0.52 (5)	+ 0.52 - 0.44 (9)	+ 1.53 - 1.01 (10)	+ 0.82 - 0.96 (24)
	U-conc.	+ 0.01 - 0.52 (5)	+ 0.49 - 0.45 (9)	+ 0.17 - 0.89 (10)	+ 0.25 - 0.68 (24)
	Pu-242/Pu-239	+ 0.16 - 0.34 (5)	+ 0.36 - 0.61 (9)	+ 0.22 - 0.99 (9)	+ 0.26 - 0.72 (23)
	Pu-conc.	+ 0.60 - 0.39 (5)	+ 0.11 - 0.65 (9)	+ 0.98 - 0.87 (9)	+ 0.47 - 0.84 (23)
	Pu-239 conc.	+ 0.54 - 0.47 (5)	+ 0.07 - 0.61 (9)	+ 0.26 - 1.04 (9)	+ 0.25 - 0.77 (23)

The figures in parentheses are the number of samples measured.

The New Brunswick Laboratory, the National Bureau of Standards (NBS) and the Central Bureau of Nuclear Measurements (CBNM, Geel) are soon to issue the 1 : 1 certified mixture of Pu-242 and Pu-239 isotopes which is needed for the calibration of plutonium measurements. CBNM can provide on request small supplies of certified mixtures (1 : 1) of enriched plutonium isotopes: IAEA-SAL has now for its own measurements a small supply of a 1 : 1 mixture of Pu-244 and Pu-239 isotopes certified by CBNM (Annex 5).

Secondly, when a mixed U and Pu tracer is used, the certification of its concentration in tracer isotopes must be based on the isotopic and element assays of the mixed tracer solution itself rather than on the assays of the source solutions of U tracer and Pu tracer, before their mixing. This precaution is necessary because the U tracer contains generally a small fraction of Pu-239 and Pu-240 isotopes which dilute the Pu-242 or Pu-244 tracer isotopes.

Another observation of importance is that precautions continue to be necessary to limit the risk of contamination of the samples. An apparent blank of about 1% of uranium was observed in the fourth experiment, but it is not possible to specify whether this blank is due to a contamination during the preparation of the resin beads or during their analyses. Dried aliquots of the tracer solutions are needed for blank measurements, as well as resin bead samples of the tracer. Considering the possibility of contamination and precision of the resin bead technique, dried aliquots of the tracer solution are needed to characterize the tracer, while resin bead samples of the tracer on each actual inspection could be used for verification of their isotopic compositions.

Significant differences in the results of the determinations of the isotopic abundances of Pu-238 and Pu-241 can be an important source of biases in the estimates of the concentration of plutonium element. The origin of the differences observed in the fourth experiment for the Pu-238 isotopic abundance merits discussion.

cont'd

To restore the desirable precision of the resin bead measurements, the mass discrimination correction must be maintained below 0.6 - 0.7% per mass unit.

Further improvements in both precision and accuracy are expected with modern automatic spectrometers with magnetic scanning (9). Multidetector instruments will probably also yield gains in precision, particularly in isotope dilution analyses.

Samples of 6 batches of spent fuel solutions have already been prepared by PNC-TRP and are available for a fifth exchange. Such an exchange will give the opportunity to test some of the recommendations made above.

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JASPAS - JC-4 - FOURTH PNC-IAEA RESIN BEAD EXPERIMENT

ANNEX 1 - PNC-TRP DATA ON THE MIXED TRACER

The measurement result of mixed tracer sample

1. Concentration of U and Pu atoms in mixed tracer solution.

U -233 2.8771×10^{15} (atoms /ml)

Pu-242 1.5022×10^{16} (atoms /ml)

2. Result of isotopic measurement number of measurements ; 10

1) U-233 (measurement date 82.9.24)

Ratio		Atom%	
R38	490.553	233	99.5303
R48	0.9248	234	0.1876
R58	0.3144	235	0.0638
R68	0.0759	236	0.0154
		238	0.2029

2) PU-242 (measurement date 82.9.30)

Ratio		Atom%	
R89	0.04395	238	0.0770
R09	1.69447	239	1.7511
R19	0.92977	240	2.9672
R29	53.4394	241	1.6281
		242	93.5767

JASPAS - JC-4 - FOURTH PNC-IAEA RESIN BEAD EXPERIMENT

ANNEX 2 - PNC-TRP DATA ON THE DILUTION AND SPIKING OF THE SAMPLES

1993 resin bead experiment at PNC-TRP.

The dilution factor and the spiking data

Batch No.	※1 1st Sampling Volume (mℓ)	※2 Diluted Volume (mℓ)	※3 Dilution Factor	※4 2nd Sampling Volume (mℓ)	Sampling Volume of mix spike (mℓ)
M12 - 050	0. 9858	149. 57	152. 72	1. 9998	2. 0205
M12 - 051	0. 9974	149. 57	150. 96	2. 0301	2. 0409
M12 - 054	1. 0011	149. 57	150. 41	2. 0200	1. 9837
M12 - 155	0. 9957	149. 57	151. 22	2. 0061	2. 0224
M12 - 058	0. 9972	149. 57	150. 99	2. 0250	2. 0051
M12 - 059	0. 9827	149. 57	153. 20	2. 0123	1. 9888
M12 - 060	0. 9999	149. 57	150. 58	2. 0120	2. 0069
M12 - 061	1. 0012	149. 57	150. 39	2. 0295	2. 0205
M12 - 063	1. 0019	149. 57	150. 29	2. 0202	2. 0176
M12 - 064	1. 0043	149. 57	149. 93	2. 0240	2. 0143

※1 Sampling from dissolver solution.

※2 Volume of 3M HNO3 used to dilute.

※3 $DF = \dfrac{\text{1st Sampling} + \text{Diluted Volume}}{\text{1st sampling}}$

※4 Sampling from diluted solution of about 150 times.

JASPAS - JC-4 - FOURTH PNC-IAEA RESIN BEAD EXPERIMENT

ANNEX 3

ISOTOPIC AND ISOTOPE DILUTION.

ANALYTICAL RESULTS OF PNC-TRP.

JASPAS - JC-4 - FOURTH PNC-IAEA RESIN BEAD EXPERIMENT

ANNEX 3 - ISOTOPIC AND ISOTOPE DILUTION ANALYTICAL RESULTS OF PNC-TRP

PNC Analytical Data — 1

(Resin Beads 4th Experiment)

		MI2 - 050	MI2 - 051	MI2 - 054	MI2 - 055	MI2 - 058	MI2 - 059	MI2 - 060	MI2 - 061	MI2 - 063	MI2 - 064
Preparation date		13.10.1982	14.10.1982	17.10.1982	18.10.1982	22.10.1982	24.10.1982	25.10.1982	26.10.1982	28.10.1982	29.10.1982
	Ratio										
U	R48	0.000154	0.000152	0.000153	0.000190	0.000212	0.000192	0.000203	0.000191	0.000177	0.000201
	R58	0.009114	0.009150	0.009156	0.010906	0.014946	0.011260	0.013035	0.011360	0.010440	0.010814
	R68	0.003145	0.003145	0.003136	0.004332	0.003847	0.003940	0.004001	0.003901	0.003421	0.004072
Pu	R89	0.024988	0.022101	0.023962	0.036102	0.024921	0.042954	0.036789	0.026856	0.041315	0.047036
	R09	0.384277	0.382881	0.381698	0.393434	0.330366	0.393325	0.357583	0.382054	0.380644	0.391054
	R19	0.188999	0.188499	0.187469	0.180772	0.140448	0.166802	0.150933	0.159883	0.182391	0.189494
	R29	0.067857	0.067454	0.066567	0.080053	0.052305	0.078318	0.062334	0.070981	0.069185	0.077037
	Atom%										
U	234U	0.01521	0.01523	0.01513	0.01867	0.02084	0.01895	0.01993	0.01885	0.01750	0.01976
	235U	0.90018	0.90371	0.90430	1.07407	1.46674	1.10892	1.28142	1.11872	1.02952	1.06530
	236U	0.31062	0.31066	0.30970	0.42657	0.37752	0.38801	0.39335	0.38415	0.33737	0.40118
	238U	98.77396	98.77039	98.77086	98.48067	98.13487	98.40412	98.30527	98.47826	98.61559	98.51373
Pu	238Pu	1.49967	1.33065	1.44378	2.13578	1.60980	2.55333	2.28836	1.63781	2.46834	2.75755
	239Pu	60.01971	60.20700	60.25212	59.15895	64.59778	59.47594	62.20337	60.98396	59.75400	58.66515
	240Pu	23.06418	23.05214	22.99806	23.27512	21.34093	23.39319	22.24252	23.29918	22.74500	22.94118
	241Pu	11.34365	11.34897	11.29533	10.69428	9.07267	9.91994	9.38829	9.75033	10.89856	11.11673
	242Pu	4.07275	4.06121	4.01069	4.73584	3.37800	4.65800	3.87743	4.32069	4.13408	4.51936

JASPAS - JC-4 - FOURTH PNC-IAEA RESIN BEAD EXPERIMENT

ANNEX 3 - ISOTOPIC AND ISOTOPE DILUTION ANALYTICAL RESULTS OF PNC-TRP

PNC Analytical Data -2

(Resin Beads 4th Experiment)

NOT STRIPPED ISOTOPICS

	M12 - 050	M12 - 051	M12 - 054	M12 - 055	M12 - 058	M12 - 059	M12 - 060	M12 - 061	M12 - 063	M12 - 064
Weight%										
U 234U	0.01496	0.01498	0.01488	0.01836	0.02049	0.01863	0.01960	0.01854	0.01721	0.01943
235U	0.88894	0.89242	0.89300	1.06069	1.44854	1.09510	1.26548	1.10478	1.01668	1.05203
236U	0.30805	0.30809	0.30713	0.42305	0.37443	0.30481	0.39012	0.30098	0.33459	0.39787
238U	98.78802	98.78450	98.78497	98.49788	98.15652	98.50145	98.32478	98.49568	98.63150	98.53065
Pu 238Pu	1.48985	1.32194	1.43434	2.12177	1.59983	2.53682	2.27397	1.62725	2.45239	2.73957
239Pu	59.87798	60.06448	60.11057	59.01859	64.46803	59.33954	62.07233	60.84586	59.61786	58.52782
240Pu	23.10614	23.09395	23.04019	23.31720	21.38733	23.43755	22.28868	23.34384	22.78828	22.98340
241Pu	11.41176	11.41705	11.36329	10.75838	9.13035	9.98025	9.44705	9.80980	10.96489	11.18369
242Pu	4.11424	4.10256	4.05159	4.78403	3.41443	4.70582	3.91793	4.37321	4.17645	4.56549
U R (83) M										
-- 1	1.07524	1.07129	1.09457	1.01397	1.06293	0.995618	1.00937	1.05503	1.08552	1.07672
-- 2	1.07538	1.07084	1.08963	1.00995	1.06066	0.996042	1.01479	1.05308	1.08295	1.07817
Pu R (92) M										
-- 1	0.982046	0.992513	0.994773	0.972917	1.01386	0.951860	0.970953	1.01018	1.00418	1.03343
-- 2	0.981769	0.997129	0.991372	0.972785	1.01253	0.953905	0.974687	1.01061	1.00933	1.03619
U (conc.) g / ℓ	190.66	186.79	185.37	177.77	183.58	173.74	175.48	181.88	187.29	185.22
Pu (conc.) g / ℓ	1.5855	1.576	1.529	1.594	1.452	1.535	1.465	1.567	1.594	1.678

JASPAS - JC-4 - FOURTH PNC-IAEA RESIN BEAD EXPERIMENT

ANNEX 4

ISOTOPIC AND ISOTOPE DILUTION ANALYTICAL RESULTS OF SAL

JASPAS - JC-4 - FOURTH PNC-IAEA RESU. AEAL EXPERIMENT
ANNEX 4 - ISOTOPIC AND ISOTOPE DILUTION ANALYTICAL RESULTS OF SAL

BATCH	DATE	LOG	$^{3}/_{8}$	$^{4}/_{8}$	$^{5}/_{8}$	$^{6}/_{8}$	LOG	$^{8}/_{9}$	$^{0}/_{9}$	$^{1}/_{9}$	$^{2}/_{9}$
		Discrim. Factor	0.9453	0.9562	0.9672	0.9781		0.9869	1.0131	1.0224	1.0315
50	83-07-11	13891		0.019	0.900	0.312	13890	0.0202	0.3871	0.1839	0.0685
	83-07-24	14145		0.020	0.898	0.313	14144	0.0199	0.3844	0.1955	0.0682
	83-07-11	13893	0.8985				13892				1.0416
	83-07-11	13895	0.9066				13894				1.0272
	83-07-24	14149	0.9123				14148				1.0329
	83-07-24	14151	0.9106				14150				1.0158
51	83-07-11	13897		0.018	0.909	0.315	13896	0.0201	0.3849	0.1838	0.0681
	84-01-05	15239		0.021	0.912	0.244	15238	0.0200	0.3851	0.1785	0.0676
	84-01-05	15241	0.8973				15240				1.0325
	84-01-05	15243	0.9152				15242				1.0260
54	83-07-25	14163		0.018	0.910	0.314	14162	0.0204	0.3843	0.1867	0.0681
	84-01-05	15245		0.019	0.894	0.310	15244	0.0202	0.3855	0.1795	0.0686
	83-07-25	14167	0.9193				14166				0.7231
	83-07-25	14153	0.8994				14152				0.7261
							14164				0.7264
	84-01-05	15247	0.8949				15246				0.7295
	84-01-09	15249	0.8902				15248				0.7225
55	83-07-25	14155		0.022	1.089	0.434	14154	0.0309	0.3964	0.1753	0.0796
	84-01-12	15279		0.025	1.088	0.437	15278	0.0307	0.3946	0.1710	0.0792
	83-07-25	14157	0.9902				14156				1.0214
	83-07-25	14159	0.9831				14158				1.0259
	84-01-12	15281	0.9736				15280				1.0249
	84-01-12	15283	0.9705				15282				1.0221
58	83-07-26	14171		0.024	1.503	0.388	14170	0.0212	0.3318	0.1371	0.0525
	84-01-12	15285		0.026	1.485	0.386	15284	0.0211	0.3341	0.1348	0.0533
	83-07-26	14173	0.9308				14172				0.9872
	84-07-13	15287	0.9134				15286				0.9936
	84-07-13	15289	0.9359				15288				0.9979

JASPAS - JC-4 - FOURTH PNC-IAEA RESIN BEAD EXPERIMENT
ANNEX 4 (cont'd) ISOTOPIC AND ISOTOPE DILUTION ANALYTICAL RESULTS OF SAL

BATCH	DATE	LOG	$^{3}/_{8}$	$^{4}/_{8}$	$^{5}/_{8}$	$^{6}/_{8}$	LOG	$^{8}/_{9}$	$^{0}/_{9}$	$^{1}/_{9}$	$^{2}/_{9}$
		Discrim. Factor	0.9453	0.9562	0.9672	0.9781		0.9869	1.0131	1.0224	1.0315
59	83-07-26	14175		0.026	1.126	0.397	14174	0.0281	0.3893	0.1736	0.0764
	84-01-02	15233		0.030	1.126	0.392	15232	0.0283	0.3902	0.1552	0.0769
	84-01-09	15251		0.031	1.126	0.399	15250	0.0280	0.3886	0.1541	0.0763
	83-07-26	14177	1.0043				14176				1.0442
	84-01-03	15235	0.9910				15234				1.0530
	84-01-05	15237	0.9939				15236				1.0434
60	83-07-26	14179		0.023	1.311	0.404	14178	0.0242	0.3646	0.1529	0.0639
	84-01-09	15253		0.026	1.328	0.401	15252	0.0227	0.3641	0.1446	0.0643
	84-01-09	15257		0.026	1.297	0.403	15256	0.0241	0.3662	0.1513	0.0653
	83-07-26	14181	0.9849				14180				1.0222
	84-01-09	15255	0.9807				15254				1.0285
	84-01-09	15259	0.9845				15258				1.0158
61	83-07-27	14185		0.022	1.142	0.393	14184	0.0260	0.3844	0.1868	0.0717
	84-01-09	15261		0.024	1.150	0.395	15260	0.0262	0.3830	0.1517	0.0710
	83-07-27	14187	0.9305				14186				0.9866
	84-01-11	15263	0.9278				15262				0.9900
	84-01-11	15271	0.9341				15270				0.9910
63							14188		0.3795	0.1812	0.0712
	83-07-27	14193		0.020	1.018	0.350	14192	0.0224	0.3811	0.1860	0.0688
	84-01-11	15265		0.023	1.024	0.354	15264	0.0229	0.3806	0.1718	0.0697
							14190				0.9938
	83-07-27	14195	0.9158				14194				0.9899
	84-01-11	15267	0.9318				15266				0.9777
	84-01-11	15269	0.9114				15268				0.9901
64	83-07-27	14197		0.025	1.073	0.406	14196	0.0272	0.3916	0.2026	0.0765
	84-01-11	15273		0.030	1.094	0.414	15272	0.0274	0.3904	0.1786	0.0760
	83-07-27	14199	0.9091				14198				0.9692
	84-01-12	15275	0.9105				15274				0.9623
	84-01-12	15277	0.9340				15276				0.9704

JASPAS - JC-4 - FOURTH PNC-IAEA RESIN BEAD EXPERIMENT

ANNEX 5

Certificate of SM 6819.

Mixture of Pu-239 and Pu-244 isotopes.

Commission of the European Communities

JOINT RESEARCH CENTRE

Geel Establishment

Central Bureau for Nuclear Measurements
Steenweg op Retie, 2440 Geel, Belgium
Tel. (014) 589421 - Telex 33589 EURAT

CERTIFICATE OF ISOTOPIC COMPOSITION

Geel, 15th March 1984

1. Applicant: Mr. S. Deron
IAEA/SAL
WIEN
Austria

2 Sample: Synthetic Mixture $^{239}Pu/^{244}Pu$

3. Results:

	Atom %	Weight %	Accuracy (2s)
^{238}Pu	0.003 5	0.003 4	± 0.000 6
^{239}Pu	53.497 0	52.996 8	± 0.045 1
^{240}Pu	1.520 4	1.512 5	± 0.003 2
^{241}Pu	0.051 3	0.051 3	± 0.001 0
^{242}Pu	0.600 9	0.602 8	± 0.001 9
^{244}Pu	44.326 9	44.833 2	± 0.045 3

Atomic Weight =

4. Reference number: SMS 6619

Atom ratio 239/244 = 1.206 9 ± 0.002 2 (2s)

5. Remarks: The sample will be stored for a minimum period of six months from the date of this certificate.

Request received at laboratory : –
Sample received at laboratory : –
Measurement achieved : –
Telephone or telex communication : –

c. P. De Bièvre

M. Gallet

International Atomic Energy Agency

IAEA/RL/134
August 1986

JASPAS Programme Task JC-4
Isotopic and Isotope Dilution Analysis of Spent Fuel Solutions by Resin Bead Mass Spectrometry

Results of the Fifth PNC-IAEA Experiment

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1. Introduction

The Resin Bead Technique for mass spectrometry offers several advantages over conventional methods. As conceived at Oak Ridge National Laboratory by Walker, and al. (1), it provides for sampling of spent fuel input solutions from reprocessing operations with a minimum of radiation exposure. This is because the resin beads only adsorb nanogram amounts of U and Pu while other actinides and fission products are washed away. In general, this technique is of interest because the low radiation levels associated with loaded resin beads would allow them to be packaged and sent by registered airmail. This would result in a significant savings in time between sampling at the facility and receipt in the Safeguards Analytical Laboratory (SAL) of the International Atomic Energy Agency in Seibersdorf, Austria.

An additional advantage of the resin bead technique is that it simplifies the mass spectrometric analysis: each resin bead can be mounted on a filament and analyzed for U and Pu isotopic content. In a similar way, samples which have been "spiked" with separated isotopes such as 233U and 242Pu can be analyzed for their U and Pu content by the isotope dilution method. A typical set of inspection samples for a particular input solution batch would consist of beads loaded with the unspiked solution and at least one set of beads loaded from a spiked mixture. These would be packaged and shipped via airmail to SAL in approximately 5 days from any facility in the world. In SAL, the beads would be unpacked and mounted directly on mass spectrometer filaments, followed by duplicate measurements and isotopic dilution calculations. The total time for sampling, shipping, analysis, and reporting of data would meet the safeguards target of 14 days for input solutions.

A number of experiments have been carried out to demonstrate the utility of the resin bead method and to document the precision and accuracy achievable. A summary of results has been given in the report of the Fourth PNC-IAEA Experiment carried out under the Japanese Support Programme for Agency Safeguards (JASPAS) Task JC-4 in cooperation with the Power and Reactor and Nuclear Fuel Development Corporation, Tokai Reprocessing Plant (PNC-TRP) (2). The results of all experiments to date have shown that the resin bead technique is capable of achieving precision and accuracy of better than 0.5% for U and Pu content of spent fuel solutions. The present experiment serves to reinforce this conclusion and to provide further operating experience with the technique. A new set of glove boxes have been installed at PNC for preparation of the resin beads. The results of this experiment show that most contamination effects have been resolved satisfactorily. Any remaining problems will be addressed in the Sixth Experiment now underway.

2. Design of the Experiment and Preparation of the Samples

A set of samples was prepared from five separate input solution batches and one rinse solution in December 1983 at PNC. An accurately measured volume of dissolver solution was taken and diluted with 3M HNO_3. An aliquot of each diluted solution (containing about 20 ug Pu and 4 mg U) was mixed with a combined 233U and 242 Pu spike prepared by PNC. The composition of the spike mixture is given in Annex 1 and the volumes of sample and spike are given in Annex 2. These spiked mixtures were subjected to an isotopic equilibration step involving reduction with Fe(II) and sulfamic acid followed by oxidation with $NaNO_2$. This treatment was used successfully in the previous three experiments. This step was followed by resin bead loading of the spiked and unspiked samples using the "batch technique" developed at ORNL (3). Figure 1 shows the overall scheme for sample preparation.

PNC also prepared resin beads and dried aliquots of their mixed spike for characterization measurements at SAL. However, it was not possible to verify the concentration of U and Pu in the spike solution. Therefore, the PNC values were used for all calculations.

The resin beads and dried spike aliquots were shipped from PNC and received in SAL in January 1985.

3. Results and Discussion

Figure 1 shows the plan for mass spectrometry measurements at SAL and PNC of the spiked and unspiked samples. Annexes 3 and 4 give the raw data of SAL for the unspiked and spiked samples, respectively. Annex 5 shows the PNC data for unspiked and spiked samples and isotope dilution results. PNC used the normal solution drop method for thermal ionization mass spectrometry, whereas SAL used an ORNL-designed 2-stage mass spectrometer (4) for resin bead measurements. The SAL measurements were performed in December 1985 through February 1986. Samples showing anomalously high Am241 were washed overnight in 8M HNO_3 to strip the Am while leaving enough Pu for good measurement.

3.1. Calibration of the Resin Bead Measurements

Standards were measured along with the input samples to verify the accuracy of the mass spectrometer. A mixture of NBS-010 U standard and NBS-947 Pu standard loaded on resin beads was used. The results of these measurements are summarized in Table 1. The Pu results are corrected to a common date (86-02-01). The average bias correction used was 0.335% per mass for U and 0.472% per mass for Pu as determined using NBS-500 standard. This bias was smaller than the 1% experienced in the Fourth Experiment and was within acceptable limits. The agreement with certified values for the major isotopes was acceptable (0.18% difference for 240/239 Pu and 0.21% difference for 235/238 U). In the case of the minor ratios of Pu, there was evidence of U interference on the 238Pu and Am interference on 241Pu. These effects have been seen in other resin bead experiments. The minor isotopes of U in the NBS-010 show a bias which is known to result from in-growth of 234 and 236U from decay of 238 and 240Pu.

3.2. Resin Bead Isotopic Analysis of the Mixed Tracer

Table 2 shows the results of measurements on the mixed tracer using the resin bead technique, compared to the PNC results obtained with the conventional solution loading method. For Pu, the reported ratios are versus 239Pu, which is a minor isotope in the spike, which causes the high CV's and relative differences. However, the effect of these differences causes a much smaller difference in the isotope dilution calculations. The same holds true for U, where the ratios are versus 238U, again a minor isotope. Because the 233/238 ratio is smaller in the SAL data, it is possible that a small 238U contamination occurred in preparing or handling the resin beads. A more accurate picture can be gained from Table 3, which shows the PNC and SAL data as atom percents. The differences on the 242Pu and 233U atom percents are within acceptable limits. A possible interference by 238U on the 238Pu shows up as a large relative difference. Similarly, the effect of 238Pu on the 238U can also be seen. Slightly higher 241Pu values in the SAL data may be due to ingrowth of 241Am.

3.3. Precision of Resin Bead Measurements

The resin bead measurements were carried out in duplicate, thus allowing an estimate of the reproducibility to be made based on the average coefficient of variation between replicate results. These data are summarized in Table 4. Compared to the Fourth PNC-IAEA Resin Bead Experiment, there was significant improvement in the precision of the spiked samples, from 0.58% to 0.25% for Pu 242/239 and from 1.05% to 0.29% for U 233/238. Other improvements included better precision for the Pu 240/239 and 242/239 as well as the U 234/238 and 235/238 in the unspiked samples. Poorer precision was obtained for 238/239 Pu due, perhaps to improper correction for the 238U interference. A definite factor contributing to better precision for the spiked samples was that the mass fractionation correction was much lower in this experiment compared to the previous one; 0.4% per mass versus over 1% per mass. Table 5 shows the individual isotope dilution results along with the averages and CV's. In cases where the original two measurements did not agree within 1% further measurements were made until the precision was acceptable. In only one case (U measurements on TK2-021) were two replicate measurements rejected.

3.4. Comparison of Isotope Dilution Measurements

Table 6 summarizes the results of SAL using the resin bead method compared to those of PNC using the conventional solution loading technique. The SAL measurements of the tracer isotopic were used throughout, along with the PNC values of U and Pu concentration in the tracer. The differences resulting from using the SAL isotopic data amounted to 0.02% for U and 0.08% for Pu. The agreement of IDA results is better than 1% which is a significant improvement over the Fourth Experiment. In fact, the average percent difference is excellent; 0.25% for Pu and −0.02% for U. This demonstrates clearly that the resin bead technique is capable of giving results of high reliability under actual inspection conditions.

4. Conclusions

This exercise has demonstrated that the resin bead method can be successfully applied to the measurement of safeguard samples with precision and accuracy approaching that of conventional mass spectrometry. The agreement between the resin bead results and those by solution loading is within the precision of the measurements and represents a significant case for using the resin bead method for routine inspection samples. Problems of isotopic interferences caused by the mixture of elements on the resin beads remain to be completely solved, but their effect on the isotope dilution results is acceptably small. The mass spectrometer used in the resin bead measurements is approaching the end of its useful life and has been superceded by more precise instruments of commercial design. These new instruments have been proven to have sufficient sensitivity to measure resin bead samples. All that remains is to develop and test measurement protocols and data reduction schemes. The resulting system will offer higher precision and accuracy for resin bead measurements.

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6. Acknowledgement

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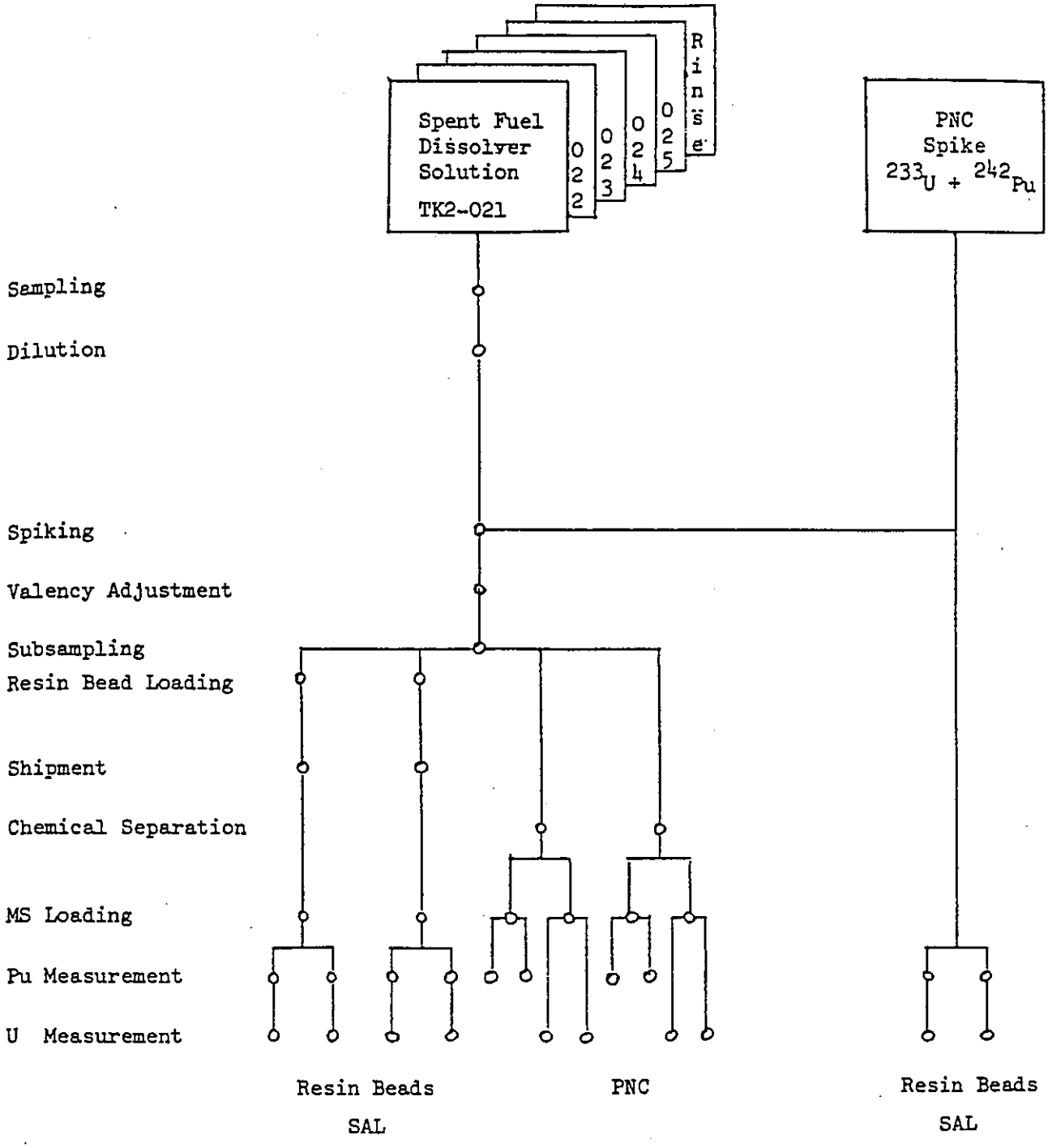

Figure 1 Schematic of Fifth PNC-IAEA Resin Bead Experiment.

Table 1 FIFTH PNC-IAEA RESIN BEAD EXPERIMENT
RESULTS OF MASS SPECTROMETRY CALIBRATIONS

Reference Material	Isotope Ratio	NBS Value 86-02-01	Measured Value 86-02-01			Discrimination Factor
			Mean	Std. Dev.	C.V. (in %)	
NBS-Pu-947	$\frac{238}{239}$	0.00349	0.00324	0.00021	6.5	0.99527
	$\frac{240}{239}$	0.24133	0.24176	0.00071	0.29	1.00472
	$\frac{241}{239}$	0.03007	0.03082	0.00063	2.0	1.00943
	$\frac{242}{239}$	0.01559	0.01563	0.00013	0.80	1.01415
NBS-U-010	$\frac{234}{238}$	0.000055	0.000071	0.000006	8.6	0.98659
	$\frac{235}{238}$	0.010145	0.010166	0.000039	0.39	0.98995
	$\frac{236}{238}$	0.000069	0.000086	0.000017	19.3	0.99330

Table 2 FIFTH PNC-IAEA RESIN BAD EXPERIMENT.
RESULTS OF ISOTOPE RATIOS OF THE TRACER.

Element	Isotope Ratio	PNC Value (83-11-10)	SAL Result (83-11-10)			Relative Diff. (in %)
			Mean	Std. Dev.	C.V. (in %)	
Plutonium	$\frac{238}{239}$	0.00070	0.03726	0.00783	21.4	98
	$\frac{240}{239}$	1.66661	1.70619	0.06604	3.9	2.3
	$\frac{241}{239}$	0.86455	0.91949	0.05885	7.1	6.0
	$\frac{242}{239}$	52.2573	53.5795	1.88351	3.5	2.5
Uranium	$\frac{233}{238}$	474.335	438.409	9.376	2.1	8.2
	$\frac{234}{238}$	0.9080	0.81730	0.01641	2.0	11.1
	$\frac{235}{238}$	0.2974	0.28483	0.01130	4.0	4.4
	$\frac{236}{238}$	0.0691	0.06374	0.00158	2.5	8.4

Table 3 FIFTH PNC-IAEA RESIN BEAD EXPERIMENT.

RESULTS OF ISOTOPIC ABUNDANCES OF THE TRACER (in atom %).

Element	Isotope	PNC Value (83-11-10)	SAL Value (83-11-10)	Relative Diff. (%)
Plutonium	238	0.00125	0.06509	98.1
	239	1.7925	1.7469	2.6
	240	2.9874	2.9805	0.23
	241	1.5497	1.6062	3.5
	242	93.6693	93.5971	0.08
	244	(0.0043) (1)	0.0041	4.9
Uranium	233	99.523	99.508	0.02
	234	0.1905	0.1855	2.7
	235	0.0624	0.0647	3.6
	236	0.0145	0.0145	0.0
	238	0.2098	0.2270	7.6

(1) Calculated using 244/239 ratio measured by SAL.

Table 4 FIFTH PNC-IAEA RESIN BEAD EXPERIMENT.

PRECISION OF RESIN BEAD MEASUREMENTS.

Element	Isotope Ratio	Average Isotope Ratio	Average CV (in %)	Number of Measurements
Plutonium	$\frac{238}{239}$	0.003523	32.4	13
	$\frac{240}{239}$	0.203331	0.063	13
	$\frac{241}{239}$	0.060124	2.78	13
	$\frac{242}{239}$	0.010747	0.78	13
Uranium	$\frac{234}{238}$	0.000173	1.36	14
	$\frac{235}{238}$	0.014964	0.49	14
	$\frac{236}{238}$	0.001532	1.42	14
Spiked Plutonium	$\frac{242}{239}$	1.41651	0.25	20
Spiked Uranium	$\frac{233}{238}$	0.96570	0.29	15

Table 5 FIFTH PNC-IAEA RESIN BEAD EXPERIMENT.

RESULTS OF ISOTOPE DILUTION MEASUREMENTS.

Sample	Pu (86-02-10) (g/l)			U (g/l)		
	Measured	Average	CV (%)	Measured	Average	CV (%)
TK2-021	0.76282 0.76259 0.76782 0.76407	0.76433	0.32	173.57 173.43	173.50	0.06
TK2-022	0.85223 0.84690 0.84963 0.84745	0.84905	0.29	193.50 190.86 193.19	192.52	0.75
TK2-023	0.87227 0.87203	0.87215	0.02	196.35 196.29	196.32	0.02
TK2-024	0.87188 0.86394 0.86159 0.86482	0.86556	0.51	197.78 199.30 200.74 198.29	199.03	0.66
TK2-025	0.90812 0.90672	0.90742	0.11	203.54 204.08	203.81	0.19
RINSE-I	0.26230 0.26045 0.26170 0.26108	0.26138	0.30	59.041 59.968	59.005	0.09

Table 6 FIFTH PNC-IAEA RESULT EXPERIMENT.
COMPARISON OF ISOTOPE DILUTION MEASUREMENTS.

Sample	Pu concentration (83-12-10) (g/l)			U concentration (g/l)		
	PNC	SAL	Diff. (%) *	PNC	SAL	Diff. (%) *
TK2-021	0.7699	0.7682	+ 0.22	173.00	173.50	- 0.29
TK2-022	0.8524	0.8534	- 0.12	192.30	192.52	- 0.11
TK2-023	0.8781	0.8766	+ 0.17	196.99	196.32	+ 0.34
TK2-024	0.8772	0.8700	+ 0.83	198.14	199.03	- 0.45
TK2-025	0.9119	0.9120	- 0.01	204.88	203.81	+ 0.52
RINSE-I	0.2638	0.2627	+ 0.42	58.93	59.01	- 0.13
Average Diff.			+ 0.25			- 0.02

* $\left(\frac{\text{PNC} - \text{SAL}}{\text{PNC}}\right) \times 100$

JASPAS - JC-4 - FIFTH PNC-IAEA RESIN BEAD EXPERIMENT

ANNEX 1 - PNC-TRP DATA ON THE MIXED TRACER

The measurement result of mixed tracer sample

(measurement date 83.11.5~11.20)

1. Concentration of U and Pu atoms in mixed tracer solution.

U -233	2.9739×10E+18 (atoms /ml)
Pu-242	1.5478×10E+16 (atoms /ml)

2. Result of isotopic measurement

1) U-233

Ratio		Atom%	
R38	474.335	233	99.523
R48	0.9080	234	0.1905
R58	0.2974	235	0.0624
R68	0.0691	236	0.0145
		238	0.2098

2) PU-242

Ratio		Atom%	
R89	0.00070	238	0.00125
R09	1.66661	239	1.7925
R19	0.86455	240	2.9874
R29	52.2573	241	1.5497
		242	93.6693

JASPAS - JC-4 - FIFHT PNC-IAEA RESIN BEAD EXPERIMENT
ANNEX 2 PNC-TRP DATA ON THE DILUTION AND SPIKING OF THE SAMPLES

1983 Resin bead experiment at PNC-TRP. The dilution factor and the spiking data

Batch No	※1 1st sampling Volume (ml)	※2 Dilutde Volume (ml)	※3 Dilution factor	※4 2nd sampling Volume (ml)	Sampling Volume of mix spike (ml)
TK2-021	0.9860	149.94	153.069	1.9666	1.9730
TK2-022	0.9784	149.94	154.250	1.9763	1.9823
TK2-023	0.9806	149.94	153.906	1.9900	1.9763
TK2-024	0.9793	149.94	154.109	1.9991	1.9677
TK2-025	0.9816	149.94	153.751	1.9763	1.9651
Rinsng - 1st	0.9854	49.98	51.721	1.9752	1.9842

※1 Sampling from dissolver solusion.

※2 Volume of 3M HNO used to dilut.

※3 $DF = \dfrac{\text{1st Sampling} + \text{Diluted Volume}}{\text{1st Sampling}}$

※ Sampling from diluted solution about 150 times.

Annex 3 FIFTH PNC-IAEA RESIN BEAD EXPERIMENT.

ISOTOPIC RESULTS OF SAL - UNSPIKED SAMPLES.

Sample	Date	Log	234/238	235/238	236/238	Log	238/239	240/239	241/239	242/239
TK2-021	85-12-12	17785	.000173	.014757	.001525	17784	.002086	.207274	.074411	.011248
	85-12-13	17786	.000169	.014812	.001523	17786	.000790	.207195	.061687	.011215
TK2-022	86-01-15	17830 *	.000136	.012399	.001346	17829 *	.053817	.204364	.064448	.011732
	86-01-30	17845	.000177	.015211	.001533	17844 *	.004091	.203834	.059881	.010838
	86-01-30	17847	.000173	.014906	.001543	17846 *	.005121	.204266	.065258	.010948
	86-02-13	17911	.000169	.015036	.001557	17910	.002556	.203948	.057946	.010939
	86-02-13	17913 *	.000230	.016545	.001592	17912	.002739	.203636	.058082	.010680
TK2-023	86-02-03	17855 *	.000166	.014966	.001537	17854 *	.004497	.203758	.081469	.010599
	86-02-03	17857	.000169	.015091	.001544	17856 *	.010978	.203957	.059311	.010767
	86-02-13	17915	.000171	.015125	.001537	17914	.002821	.203747	.058407	.010991
	86-02-18	17919	.000172	.015138	.001517	17918	.002467	.203550	.058301	.010781
TK2-024	86-02-06	17875	.000181	.015025	.001554	17874 *	.003990	.202614	.103757	.010784
	86-02-06	17877	.000180	.015032	.001571	17876 *	.006130	.201835	.140207	.010702
						17949	.002995	.201644	.057472	.010660
						17950	.003536	.201765	.059509	.010533
						17951	.003169	.201427	.057577	.010371
TK2-025	86-02-07	17883	.000171	.015015	.001429	17882	.012798	.201606	.059693	.010449
	86-02-07	17887	.000165	.014878	.001540	17886	.002596	.201412	.058730	.010456
Rinse I	86-02-11	17895	.000170	.014939	.001549	17894	.003140	.202216	.058905	.010567
	86-02-11	17897	.000171	.014767	.001534	17896	.003818	.202160	.058957	.010593

* NOT USED IN CALCULATIONS

ANNEX 4 FIFTH PNC-IAEA RESIN BEAD EXPERIMENT.
ISOTOPIC RATIOS OF SAL - SPIKED SAMPLES.

Batch	Date	Log	233/238	Date	Log	242/239
TK2-021	86-01-02	17805	1.054510	86-01-02	17805	1.559827
	86-01-02	17807	1.055343	86-01-02	17808	1.560277
				86-02-18	17920	1.550029
				86-02-18	17922	1.557369
TK2-022	86-02-03	17851	.952818	86-01-31	17850	1.401648
	86-02-03	17853	.965978	86-02-03	17852	1.410181
	86-02-20	17933	.954359	86-02-20	17932	1.405788
	86-02-21	17935	.926342	86-02-21	17934	1.409284
TK2-023	86-02-03	17859	.928362	86-02-03	17858	1.359735
	86-02-04	17863	.928624	86-02-04	17862	1.360086
TK2-024	86-02-06	17879	.914682	86-02-06	17878	1.337071
	86-02-07	17881	.907688	86-02-06	17880	1.348964
	86-02-19	17927	.901191	86-02-19	17926	1.352522
	86-02-20	17931	.912333	86-02-20	17930	1.347641
TK2-025	86-02-10	17891	.895631	86-02-10	17890	1.302564
	86-02-10	17893	.893265	86-02-10	17892	1.304518
Rinse I	86-02-12	17901	1.048991	86-02-12	17900	1.520278
	86-02-12	17903	1.050278	86-02-12	17902	1.530718
				86-02-27	17952	1.523618
				86-02-27	17953	1.527138

JASPAS - JC-4 - FIRST PNC-IAEA RESIN BEAD [illegible]IMENT
ANNEX 5 PNC-TRP DATA ON THE DILUTION AND S[illegible]KING OF THE SAMPLES
PNC Analytcal Data - 1 (Resin beads 5th Expeiment)

	TK2-021	TK2-022	TK2-023	TK2-024	TK2-025	Rinsing - 1st
Preparation data	06. 12. 83	07. 12. 83	08. 12. 83	09. 12. 83	10. 12. 83	11. 12. 83
U Rasio						
R48	0. 000167	0. 000163	0. 000163	0. 000163	0. 000163	0. 000163
R58	0. 014810	0. 014810	0. 014945	0. 014971	0. 014904	0. 014904
R68	0. 001515	0. 001525	0. 001535	0. 001554	0. 001545	0. 001555
Pu Rasio						
R89	0. 002958	0. 002858	0. 002897	0. 002865	0. 002877	0. 002867
R09	0. 206631	0. 204235	0. 203807	0. 201770	0. 201576	0. 202066
R19	0. 065357	0. 064455	0. 064436	0. 063638	0. 064033	0. 064309
R29	0. 011112	0. 010740	0. 010665	0. 010370	0. 010384	0. 010534
U Atom%						
234U	0. 016	0. 016	0. 016	0. 016	0. 016	0. 016
235U	1. 457	1. 464	1. 470	1. 474	1. 466	1. 466
236U	0. 149	0. 150	0. 151	0. 153	0. 152	0. 153
238U	98. 378	98. 370	98. 363	98. 457	98. 366	98. 365
Pu Atom%						
238Pu	0. 230	0. 223	0. 226	0. 224	0. 225	0. 224
239Pu	77. 757	78. 023	78. 015	78. 208	78. 194	78. 138
240Pu	16. 067	15. 887	15. 900	15. 780	15. 762	15. 789
241Pu	5. 082	5. 029	5. 027	4. 977	5. 007	5. 025
242Pu	0. 684	0. 838	0. 832	0. 811	0. 812	0. 823

JASPAS - JC-4 - FIFHT PNC-IAEA RESIN BEAD EXPERIMENT
ANNEX 5 PNC-TRP DATA ON THE DILUTION AND SPIKING OF THE SAMPLES

PNC Analytcal Data - 2 (Resin beads 5th Expeiment)

	TK2-021	TK2-022	TK2-023	TK2-024	TK2-025	Rinsing - 1st
U Weight%						
234U	0.016	0.016	0.016	0.016	0.016	0.016
235U	1.439	1.445	1.452	1.456	1.448	1.448
236U	0.148	0.149	0.150	0.151	0.151	0.151
238U	98.397	98.390	98.382	98.377	98.385	98.385
Pu Weight%						
238Pu	0.229	0.222	0.225	0.233	0.224	0.223
239Pu	77.664	77.931	77.922	78.117	77.102	78.047
240Pu	16.114	15.935	15.948	15.828	15.810	15.836
241Pu	5.119	5.065	5.064	5.013	5.043	5.062
242Pu	0.874	0.847	0.841	0.819	0.821	0.832
U R (83) M						
-1	0.946415	1.041930	1.096930	1.096930	1.119766	0.94950
-2	0.943758	1.042789	1.093476	1.093476	1.117367	0.95365
Pu R (92) M						
-1	0.649006	0.712282	0.744259	0.748745	0.767358	0.660429
-2	0.647503	0.712901	0.739421	0.748525	0.768493	0.658697
U (CONC) g/l	173.00	192.30	196.99	198.14	204.88	58.93
Pu (conc) g/l	0.7699	0.8524	0.8781	0.8772	0.9119	0.2638

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JASPAS Programme Task JC-4
Isotopic and Isotope Dilution Analysis of Spent Fuel Solutions by Resin Bead Mass Spectrometry

Results of the Sixth Interlaboratory Experiment

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1. Introduction

The use of resin beads for mass spectrometry of U and Pu has been extensively developed at Oak Ridge National Laboratory in the U.S.A. and tested in a number of intercomparison experiments between the Safeguards Analytical Laboratory (SAL) of the IAEA and the Power Reactor and Nuclear Fuel Development Corporation (PNC) - Tokai Reprocessing Plant (TRP) in Japan. The latest progress in the implementation of this technique can be found in the report of the 5th IAEA PNC Intercomparison Exercise (1). The goal of such exercises has been to demonstrate the precision and accuracy which can be obtained with this technique compared to the more conventional method of solution deposition on the mass spectrometer filament. Resin beads represent a convenient way to concentrate the U and Pu in spent fuel dissolver solution samples from reprocessing facilities, with the added advantage that fission product elements and other actinides such as Am are removed. The result is that the small amount of radioactivity present in typical resin bead samples allows them to be shipped in airmail packages, with a considerable saving in time and expense compared to the type-A containers which are currently used for spent fuel inspection samples.

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Previous exercises in this programme have shown that the precision and accuracy of resin bead measurements performed at SAL are acceptable and compare well with conventional mass spectrometry procedures. Some difficulties in preventing contamination of the samples have been overcome by the facility operator, and a new glove-box for resin bead preparation was placed into operation for this 6th exercise. Further improvements can be expected from the use of a robot system for the chemical processing and bead preparation steps.

For the first time in this 6th exercise, the operator's laboratory (PNC) and the state Safeguards laboratory (NMCC) have undertaken to make resin bead measurements in parallel with those of SAL. This represents a major step forward because of the possibility of comparing results from the operator, the state safeguards authority, and the IAEA on the same samples in order to detect problems in the preparation of the IAEA samples. An additional step toward identifying significant error sources would be the use of a common tracer (spike) between all 3 laboratories. Also remaining to be improved is the actual shipment conditions for resin bead samples to fully exploit their advantages.

2. Design of the Experiment and Preparation of the Samples

A set of samples consisting of 4 dissolver batches and 1 rinse batch were taken from the 85-1-C campaign at PNC/TRP in May 1985. The concentrated spent fuel solutions were diluted by volume (approximate dilution factor = 150). From the diluted samples, an aliquot was taken and loaded on anion exchange resin beads to serve as unspiked samples. Another aliquot was taken and spiked with a solution containing 233 U and 242 Pu prepared and characterized by PNC/TRP. Following a chemical equilibration step, the spiked aliquots were also loaded on resin beads. The resin beads were loaded in a bulk preparation process which was developed at ORNL (2) and which resulted in approximately 1000 resin beads for each sample. Portions of these containing about 100 beads were removed for each of the 3 participating laboratories. The complete scheme is shown in Figure 1 and described in Annex A.

In addition, it was decided that each laboratory should measure the isotopic composition and concentration of the 233 U and 242 Pu in the mixed tracer. This was done by drying accurately measured aliquots of the tracer solution in glass bottles which were then distributed to the 3 labs. One aliquot was used as an unspiked sample and the remaining 5 were mixed with a chemical standard in each lab, followed by IDA analysis. The scheme for the dried tracer preparation and measurements is shown in Figure 3. Finally, an aliquot of the tracer mixed with the PNC/TRP chemical standard was loaded on resin beads and separate portions containing about 100 beads each were sent to SAL for controlling the mass fractionation correction factor. This preparation is shown in Figure 2.

The dried tracer and resin bead samples were shipped from PNC/TRP and received in SAL in November 1985.

3. Results and Discussion

Measurements on the resin bead samples at SAL were performed on the ORNL-designed 2-Stage Mass Spectrometer. For the dried tracer samples, the U measurements were obtained on the VG54E instrument and the Pu results were obtained with the Finnigan MAT 261 of SAL. PNC/TRP used a VG54 mass spectrometer and obtained their mass fractionation correction factor for the resin bead measurements from the mixed tracer plus chemical standard resin bead samples. NMCC used their MAT 260 instrument and obtained the fractionation correction factor from resin bead standards provided with the TIGR-82 programme. Both PNC/TRP and NMCC reported problems with obtaining a sufficient ion beam intensity with the resin bead samples. This problem was overcome by both labs and further improvements in the loading and measurement techniques can be expected to yield even better results.

The SAL measurements were performed in March-May 1986.

3.1. Conventional Measurements of the Tracer

Table 1 contains the results of the SAL measurements on the PNC/TRP tracer containing 233 U and 242 Pu. The isotopic measurements are shown in Table 1 a and the U and Pu assay measurements are shown in Table 1 b. A mixed chemical standard was used for the assay measurements which contained known amounts of NBS-949 Pu and NBS-960 U. Five aliquots of the dried tracer (T001-T005) were mixed with the chemical standard and submitted to replicate mass spectrometry measurements.

Table 2 shows the PNC/TRP results for the characterization of the tracer. The isotopic results are given in Table 2 a and the U and Pu assay results are shown in Table 2 b. NMCC did not perform a complete analysis of the tracer, but reported only verification measurements which are shown in Table 3. A comparison of conventional vs resin bead measurements for characterization of the tracer will be presented later in a summary table.

3.2. Resin Bead Measurements of the Tracer

Only SAL measured the tracer loaded on resin beads; the results of the U and Pu assay measurements using the PNC/TRP mixed chemical standard are shown in Table 4. Comparison of these results with the conventional measurements of PNC/TRP shows a bias of +1.49 % for Pu and -1.67 % for U. This can be converted into a residual fractionation bias of 0.496 % /mass for Pu and 0.334 % / mass for U.

3.3. Conventional Measurements of the Samples

PNC/TRP reported the results of their conventional measurements on the 5 spent fuel samples. The data are summarized in Tables 5 (isotopic results) and 6 (U and Pu assay results).

3.4. Resin Bead Measurements of the Samples

The SAL results for the resin bead measurements of the samples are shown in Table 7 (isotopic results), Table 8 (U and Pu assay results using the SAL Resin Bead tracer characterization), and Table 9 (U and Pu assay results using the PNC/TRP conventional tracer values). The assay results were calculated in two ways:

1. Using the results of the resin bead measurements of the tracer to correct for the residual fractionation bias, assuming that this bias is the same for all resin bead measurements. It has already been noted that there was a residual bias on the resin bead measurements of the tracer between 0.3 and 0.5 % per mass unit.

2. Using the conventional tracer characterization data. This assumes that the resin bead measurements of the samples are unbiased, which is the normal assumption in the absence of other evidence, because an average bias correction factor has been applied to the data based on standard measurements.

Table 10 shows the PNC/TRP results for the resin bead measurements of the samples, while Table 11 gives the U and Pu assay results using their own conventional tracer characterization.

The resin bead results of NMCC are given in Table 12 (isotopic results) and Table 13 (U and Pu assay using the PNC/TRP conventional tracer characterization).

3.5. Summary of Results and Evaluation

Table 14 shows a comparison of the results of the conventional tracer characterization measurements. The isotopic results are given as average of all measurements at each lab and corrected to a common date of reference (85-01). The mean concentrations of 233 U and 242 Pu are shown along with the relative standard deviation and number of measurements for each lab. It can be seen that the precision for the SAL resin bead measurements is quite good and is comparable to the SAL conventional results. The NMCC results are from only a single measurement and do not reveal the precision of analysis. The PNC/TRP data show very good precision.

Table 15 gives a summary of the results for the 5 input samples from all 3 labs using resin bead loading compared to the operator's conventional measurements. The Pu data have been corrected to common date of reference (85-07-25). The NMCC and PNC/TRP resin bead assay results were calculated with the PNC/TRP conventional tracer characterization, as were one of the sets of SAL data.

Table 16 shows the relative deviations of the data in Table 15 from the reference value (PNC/TRP conventional measurements). The PNC/TRP resin bead results show a consistent negative bias for U and a corresponding positive bias for Pu, indicating that insufficient fractionation bias correction has been applied. The NMCC results show a similar pattern with consistently higher U and lower Pu results, which is likely to be due to too much bias correction being applied.

The SAL resin bead results using the PNC/TRP tracer data are in better agreement, with the operator's values, with a mean bias of + 0.10 % for U and 0.43 % for Pu (including one anomalous result for FU1-033). This conclusion is consistent with the results of previous resin bead exercises. What is not clear is the higher bias observed when the SAL resin bead results for the tracer are used in the IDA calculations. There was obviously a significant difference between the residual bias encountered with the sample and tracer measurements on resin beads. It seems that the sample measurements showed little of the 0.3-0.5 % per mass bias which was seen in the tracer data.

4. Conclusions

This exercise has further demonstrated that the resin bead sampling method can provide results of sufficient quality for safeguards purposes. The problems of sample contamination seen in previous exercises has been brought under control by the use of a dedicated glove-box for bead preparation at PNC/TRP and by use of the 'bulk' loading procedure developed at ORNL. Further work on an automated system for sample preparation and resin bead loading will be carried out under the JASPAS programme. This experiment has also demonstrated that two other labs, PNC/TRP and NMCC are able to make resin bead measurements with their commercial mass spectrometers. However it should be noted that precise analysis on resin bead measurement still requires a specialist because of the difficulty of the measurement. The remaining problems of fractionation bias correction can be solved by further investigations and method development.

5. References

1. K. Onishi, et.al., JASPAS Programme Task JC-4, Isotopic and Isotope Dilution Analysis of Spent Fuel Solutions by Resin Bead Mass Spectrometry, Results of the Fifth PNC-IAEA Experiment, IAEA/RL/134, August 1986.

2. R.L. Walker, et. al., Resin Beads as a Sample Acquisition and Loading Medium for Mass Spectrometric Analysis, ORNL/TM-5505/R1, September 1985.

Table 1 a SAL Conventional Mass Spectrometry
Results for isotopic composition of dry spike samples

Element	Sample No.	Isotopic Ratio	Measurement 1	Measurement 2	Measurement 3	Mean	Date
U	T006	233/238	447.9490	445.5680	446.5840	446.0340	86-05
		234/238	.8381	.8144	.8198	.8241	86-05
		235/238	.2832	.2754	.2765	.2784	86-05
		236/238	.0650	.0634	.0632	.0639	86-05
Pu	T006	238/239	.0208 / .2500	.0211 / .0238	.0196	.0221	86-05
		240/239	1.8631 / 1.8624	1.8760 / 1.8416	1.8545	1.8595	86-05
		241/239	.8527 / .8520	.8530 / .8471	.8505	.8511	86-05
		242/239	58.6739 / 58.7691	58.9249 / 58.2279	58·4721	58·6136	86-05
		244/239	.0025 / .0000	.0025 / .0041	.0064	.0032	86-05

Table 1 b SAL Conventional Mass Spectrometry Results for dry spike solution

Element	Sample No.	Date	U-233 atoms/1 ml spike soln.	Mean at/ml
U	T001	86-05	2.71294×10^{18} 2.71013×10^{18}	2.7157×10^{18}
	T002	86-05	2.71471×10^{18} 2.71343×10^{18}	
	T003	86-05	2.71533×10^{18} 2.71538×10^{18}	
	T004	86-05	2.72267×10^{18} 2.72114×10^{18}	
	T005	86-05	2.71621×10^{18} 2.71503×10^{18}	
Pu	T001	86-05	1.52474×10^{16} 1.52811×10^{16}	1.5336×10^{16}
	T002	86-05	1.53636×10^{16} 1.53269×10^{16}	
	T003	86-05	1.53849×10^{16} 1.53556×10^{16}	
	T004	86-05	1.53639×10^{16} 1.53904×10^{16}	
	T005	86-05	1.53113×10^{16} 1.53369×10^{16}	

Table 2 a PNC Conventional Mass Spectrometry
Results isotopic composition of dry spike sample

Element	Sample No.	Isotopic Ratio	Measurement 1	Measurement 2	Measurement 3	Mean	Date
U	T006	233/238	485·9950	485·9410	482·9411	484.9490	85-01
		234/238	0.9282	0.9265	0.8726	0.9091	85-01
		235/238	0.3007	0.3112	0.2896	0.3005	85-01
		236/238	0.0697	0.0693	0.0699	0.0697	85-01
Pu	T006	238/239	.0297	0.0274	0.0237	0.0269	85-01
		240/239	1.8459	1.8465	1.8448	1.8457	85-01
		241/239	0.9109	0.9245	0.9288	0.9214	85-01
		242/239	58·6619	58.7313	58.6971	58.6968	85-01

Table 2 b PNC Conventional Mass Spectrometry Results for characterization of dry spike solution

Element	Sample No.	Date	U-233 atoms/1 ml spike soln.	Mean at/ml
U	T001	85-01	2.7046×10^{18}	
	T002	85-01	2.7047×10^{18}	
	T003	85-01	2.7045×10^{18}	2.7045
	T004	85-01	2.7044×10^{18}	$\times 10^{18}$
	T005	85-01	2.7042×10^{18}	
			Pu-242 atoms/ 1 ml spike soln	
Pu	T001	85-01	1.5303×10^{16}	
	T002	85-01	1.5300×10^{16}	
	T003	85-01	1.5307×10^{16}	1.5303
	T004	85-01	1.5301×10^{16}	$\times 10^{16}$
	T005	85-01	1.5302×10^{16}	

Table 3

NMCC Conventional Measurements - Tracer

U

	233	234	235	236	238
at. %	99.558	.179	.054	.008	.200

233 U atoms/ml = 2.7320 E18

Pu

	238	239	240	241	242	244
at. %	.035	1.615	2.964	1.367	94.018	.001

242 Pu atoms/ml = 1.5300 E16

Table 4

SAL Resin Bead Measurements - Tracer + Chemical Standard

Sample	Date	242 Pu (at / ml)	233 U (at / ml)
9617-06-11	86-03-20	1.5558 E16	2.6666 E18
		1.5571	2.6666
9617-06-12		1.5582	2.6602
		1.5507	2.6597
9617-06-13		1.5483	2.6527
		1.5555	2.6656
9617-06-14		1.5471	2.6542
		1.5522	2.6545
	mean	1.5531 E16	2.6600 E18
	SD	.0041	.0058
	RSD	.27 %	.22 %

Table 5: PNC Conventional Mass Spectrometry Results for input Samples

JASPAS-JC-4 SIXTH IAEA-NMCC-PNC RESIN BEAD EXPERIMENT

ISOTOPIC AND ISOTOPE DILUTION ANALYTICAL RESULTS OF PNC (Pu)

Preparation date	FU2-020 18-07-85	FU2-022 19-07-85	FU2-033 25-07-85	FU2-034 26-07-85	1st-Rinsing 30-07-85
Pu Ratio					
R 89	0.012412	0.013530	0.026653	0.024676	0.025085
R 09	0.331017	0.336997	0.441462	0.428585	0.434343
R 19	0.108331	0.110173	0.165957	0.163837	0.164815
R 29	0.042247	0.042468	0.085403	0.081290	0.085428
Pu Atom %					
238	0.831	0.900	1.550	1.453	1.467
239	66.934	66.526	58.157	58.879	58.491
240	22.156	22.419	25.674	25.235	25.405
241	7.251	7.329	9.652	9.647	9.640
242	2.828	2.826	4.967	4.786	4.997
Pu Weight %					
238	0.826	0.895	1.540	1.443	1.458
239	66.810	66.402	58.015	58.738	58.348
240	22.208	22.471	25.719	25.280	25.050
241	7.298	7.377	9.709	9.704	9.697
242	2.858	2.855	5.017	4.835	5.047
Pu R (92) M					
-1	0.901588	0.915025	0.888534	0.901712	0.496176
-2	0.900446	0.920347	0.891707	0.900004	0.496468
Pu (Conc. g/l)					
-1	1.227	1.263	1.454	1.523	0.267
-2	1.226	1.270	1.460	1.520	0.267

Table 6: PNC Conventional Mass Spectrometry Results for input samples

JASPAS-JC-4 SIXTH IAEA-NMCC-PNC RESIN BEAD EXPERIMENT

ISOTOPIC AND ISOTOPE DILUTION ANALYTICAL RESULTS OF PNC (U)

Preparation date	FU2-020 18-07-85	FU2-022 19-07-85	FU2-033 25-07-85	FU2-034 26-07-85	1st-Rinsing 30-07-85
U Ratio					
R 48	0.000133	0.000138	0.000121	0.000122	0.000116
R 58	0.011839	0.011622	0.008178	0.008192	0.007966
R 68	0.002615	0.002698	0.003150	0.003153	0.003197
U Atom %					
234	0.013	0.013	0.012	0.012	0.012
235	1.167	1.146	0.809	0.810	0.788
236	0.258	0.266	0.314	0.312	0.316
238	98.562	98.575	98.865	98.866	98.884
U Weight %					
234	0.013	0.013	0.012	0.012	0.011
235	1.152	1.131	0.798	0.800	0.778
236	0.256	0.264	0.312	0.309	0.314
238	98.579	98.592	98.878	98.879	98.897
U R (83) M					
-1	1.138518	1.152019	1.150106	1.139368	0.557401
-2	1.135915	1.153854	1.150249	1.131936	0.557164
U (Conc. g/l)					
-1	180.9	184.2	182.8	189.7	30.71
-2	180.5	184.5	182.8	188.5	30.70

Table 7a IAEA-SAL, Resin Bead Results for Input Samples

Uranium Isotopic Composition

Batch Name	Sample No.	Date	Measurement No.	U Ratio 234/238	U Ratio 235/238	U Ratio 236/238
Fu2-020	001	86-3	1	.00016	.01207	.00264
			2	.00016	.01173	.00255
Fu2-022	003	86-3	1	.00018	.01163	.00267
			2	.00015	.01162	.00270
Fu2-033	005	86-3	1	.00017	.00813	.00316
			2	.00017	.00822	.00318
			3	.00015	.00817	.00319
Fu2-034	007	86-3	1	.00015	.00821	.00317
			2	.00015	.00817	.00317
			3	.00017	.00818	.000065*
Rinsing	009	86-3	1	.00018	.00802	.00321
			2	.00020	.00843	.00320
			3	.00014	.00794	.00319

Batch Name	Sample No.	U Mean Wt. % 234	235	236	238
Fu2-020	001	.0155	1.1582	.2536	98.5727
Fu2-022	003	.0160	1.1316	.2625	98.5899
Fu2-033	005	.0159	.7979	.3114	98.8747
Fu2-034	007	.1152	.7992	.3108	98.8747
Rinsing	009	.0168	.7937	.3137	98.8757

* omitted

Table 7b IAEA-SAL Resin Bead Results
for Input Samples

Plutonium Isotopic Composition

Batch Name	Sample No.	Date	Measurement No.	Pu Ratio 238/239	240/239	241/239	242/239
Fu2-020	001	86-3	1	.01426	.32938	.10613	.04213
			2	.01362	.32856	.11682	.04233
Fu2-022	003	86-3	1	.01349	.33809	.10788	.04295
			2	.01363	.33691	.10655	.04225
Fu2-033	005	86-3	1	.02673	.44114	.16312	.08535
			2	.02628	.44127	.16541	.08552
			3	.04041	.44155	.16936	.08540
Fu2-034	007	86-3	1	.03067	.42837	.16060	.08148
			2	.01347	.42791	.16158	.08502
			3	.02600	.42821	.15791	.08110
Rinsing	009	86-3	1	.02593	.43444	.16522	.08533
			2	.02372	.43402	.16161	.08536

Batch Name	Sample No.	Pu Mean Wt % 238	239	240	241	242
Fu2-020	001	.9258	66.6933	22.0320	7.4970	2.8519
Fu2-022	003	.8980	66.5041	22.5392	7.1900	2.8687
Fu2-033	005	1.7956	57.8687	25.6456	9.6846	5.0055
Fu2-034	007	1.3710	58.8865	25.3187	9.5026	4.9212
Rinsing	009	1.4440	58.4121	25.4706	9.6255	5.0479

Table 8: IAEA-SAL IDMS results for Input Samples (Using SAL-RB Tracer Results)

Batch Name	Sample No.	Date	Measurement No	Isotopic Ratio		Concentration	
				U 233/238	Pu 242/239	U (g/l)	Pu (g/l)
Ful-020	001S	86-3	1	.86883	1.11337	179.894	1.2432
			2	.86668	1.11329	180.342	1.2433
	002S	86-3	1	.87708	1.11361	178.199	1.2429
			2	.87392	1.11113	178.845	1.2458
			3		1.11099		1.2460
Ful-033	003S	86-3	1	.86456	1.09377	181.884	1.2785
			2	.86752	1.08555	181.263	1.2887
			3		1.09032		1.2828
	004S	86-3	1	.85210	1.09670	184.549	1.2749
			2	.86337	1.08815	182.137	1.2855
			3	.86707	1.08533	181.359	1.2890
Ful-033	005S	86-3	1	.87395	1.11326	178.195	1.4920
			2	.86963	1.11703	179.082	1.4864
	006S	86-3	1	.86238	1.10677	180.590	1.5016
			2	.85798	1.11169	181.518	1.4943
Ful-034	007S	86-3	1	.88832	1.10998	184.295	1.5430
			2	.88748	1.10122	184.470	1.5565
	008S	86-3	1	.87899	1.11249	186.255	1.5392
			2	.88049	1.10365	185.936	1.5528
Rinsing	009S	86-3	1	1.80074	2.01873	30.105	.26973
			2	1.80998	2.01711	29.950	.26996
	010S	86-3	1	1.80117	2.01799	30.098	.26984
			2	1.80803	2.01652	29.983	.27005

Table 9 SAL Resin bead IDM Results for Input Samples (using PNC Tracer Results)

Batch Name	Sample No.	Measure-ment No.	Concentration U (g/l)	Concentration Pu (g/l)
Ful-020	001S	1	182.904	1.2249
		2	183.359	1.2250
	002S	1	181.180	1.2247
		2	181.837	1.2276
		3	181.837	1.2277
Ful-033	003S	1	184·927	1.2597
		2	184.295	1.2698
		3		1.2640
	004S	1	187.636	1.2562
		2	185.184	1.2666
		3	184.393	1.2701
Ful-033	005S	1	181.176	1.4701
		2	182.078	1.4646
	006S	1	183.611	1.4796
		2	184.555	1·4724
Ful-034	007S	1	187.378	1.5204
		2	187.556	1.5337
	008S	1	189.371	1.5166
		2	189·047	1·5300
Rinsing	009S	1	30.609	.26577
		2	30.451	.26600
	010S	1	30.602	.26588
		2	30.485	·26609

Table 10 a PNC Resin Bead Results
for Input Samples

Uranium Isotopic composition

Batch Name	Sample No.	Date	Measure-ment No.	U Ratio		
				234/238	235/238	236/238
Fu2-020	001	86-05-22	1	0.000156	0.016077	0.002611
			2	0.000150	0.013718	0.002616
Fu2-022	003	86-05-22	1	0.000157	0.011702	0.002678
			2	0.000149	0.011863	0.002681
Fu2-033	005	86-05-26	1	0.000141	0.008330	0.003154
			2	0.000143	0.008199	0.003170
Fu2-034	007	86-05-26	1	0.000128	0.008610	0.003119
			2	0.000092	0.008476	0.003137
Rinsing	009	86-05-26	1	0.000134	0.007940	0.003183
			2	0.000131	0.008325	0.003190

Batch Name	Sample No.	U Mean Wt. %			
		234	235	236	239
Fu2-020	001	0.015	1.446	0.255	98.284
Fu2-022	003	0.015	1.147	0.262	98.576
Fu2-033	005	0.014	0.807	0.312	98.867
Fu2-034	007	0.011	0.834	0.307	98.848
Rinsing	009	0.013	0.794	0.312	98.881

Table 10 b IAEA-SAL Resin Bead Results
for Input Samples

Plutonium Isotopic Composition

Batch Name	Sample No.	Date	Measure-ment No.	Pu Ratio 238 * / 239	240 / 239	241 / 239	242 / 239
Fu2-020	001	86-05-22	1	0.012412	0.326481	0.103326	0.045730
			2	0.012412	0.326217	0.101556	0.042514
Fu2-022	003	86-05-22	1	0.013530	0.336555	0.104864	0.042343
			2	0.013530	0.335250	0.104199	0.041772
Fu2-033	005	86-05-26	1	0.026653	0.437877	0.157383	0.083664
			2	0.026653	0.438157	0.157165	0.083693
Fu2-034	007	86-05-26	1	0.024676	0.425766	0.155655	0.080936
			2	0.024676	0.425438	0 155679	0.079932
Rinsing	009	86-05-26	1	0.025085	0.432619	0.157353	0.085400
			2	0.025085	0.431117	0.155658	0.083576

Batch Name	Sample No.	Pu Mean Wt % 238*	239	240	241	242
Fu2-020	001	0.831	67.202	22.023	6.942	3.002
Fu2-022	003	0.899	66.721	22.506	7.033	2.841
Fu2-033	005	1.552	58.489	25.727	9.276	4.956
Fu2-034	007	1.454	59.158	25.284	9.287	4.818
Rinsing	009	2.468	57.754	25.480	9.272	5.026

* alpha spectrometry measurement

Table 11 PNC Resin Bead IDM
Results for Input
Samples

Batch Name	Sample No.	Date	Measure-ment No	Isotopic Ratio		Concentration	
				U 233/238	Pu 242/239	U (g/l)	Pu (g/l)
Ful-020	001S	86-05-19	1	0.8887	1.0882	179.3	1.248
			2	0.8931	1.0938	179.5	1.241
	002S	86-05-19	1	0.8875	1.0942	179.6	1.240
			2	0.8812	1.1006	180.9	1.233
Ful-022	003S	86-05-19	1	0.8757	1.0746	182.6	1.277
			2	0.8754	1.0864	182.7	1.264
	004S	86-05-19	1	0.8808	1.0792	181.6	1.273
			2	0.8765	1.0758	182.4	1.207
Ful-033	005S	86-05-20	1	0.8756	1.1040	181.5	1.467
			2	0.8772	1.1129	181.2	1.453
	006S	86-05-20	1	0.8588	1.1071	185.1	1.463
			2	0.8693	1.1150	181.2.	1.451
Ful-034	007S	86-05-20	1	0.8879	1.0994	187·6	1.526
			2	0.8879	1.1086	187.6	1.512
	008S	86-05-20	1	0.8901	1.0967	185.1	1.530
			2	0.8904	1.0997	187.0	1.525
Rinsing	009S	86-05-21	1	1.7985	1.9926	30.65	0.269
			2	1.7883	1.9930	30.82	0.269
	010S	86-05-21	1	1.8111	1.9942	30.43	0.269
			2	1.8106	1.9961	30·44	0.267

Table 12 a NMCC Resin Bead Results
for Input Samples

Uranium Isotopic Composition

Batch Name	Sample No.	Date	Measure-ment No.	U Ratio		
				$\frac{234}{238}$	$\frac{235}{238}$	$\frac{236}{238}$
Fu2-020	001	5/14	1	0.000147	0.0117	0.00262
			2	0.000145	0.0117	0.00260
Fu2-022	003	5/1	1	0.000154	0.0116	0.00267
			2	0.000150	0.0115	0.00268
Fu2-033	0.05	5/1	1	0.000147	0.00805	0.00313
			2	0.000150	0.00808	0.00314
Fu2-034	0.07	5/7	1	0.000147	0.00809	0.00312
			2	0.000151	0.00811	0.00313
Rinsing	009	5/8	1	0.000151	0.00791	0.00315
			2	0.000149	0.00788	0.00318

Batch Name	Sample No.	U Mean Wt %			
		234	235	236	238
Fu2-020	001	0.014	1.140	0.255	98.591
Fu2-022	003	0.015	1.125	0.262	98.599
Fu2-033	005	0.015	0.788	0.308	98.891
Fu2-034	007	0.015	0.791	0.307	98.888
Rinsing	009	0.015	0.771	0.311	98.905

Table 12b NMCC Resin Bead Results for Input Samples

Plutonium Isotopic Composition

Batch Name	Sample No.	Date	Measurement No.	U Ratio 238/239	U Ratio 240/239	U Ratio 241/239	U Ratio 242/239
Fu2-020	001	5/14	1	0.0682	0.3267	0.1027	0.0417
			2	0.0229	0.3270	0.1026	0.0419
Fu2-022	003	5/1	1	0.0139	0.3367	0.1056	0.0429
			2	0.0135	0.3367	0.1053	0.0424
Fu2-033	005	5/1	1	0.0244	0.4410	0.1593	0.0852
			2	0.0278	0.4403	0.1596	0.0847
Fu2-034	007	5/7	1	0.0239	0.4273	0.1572	0.0811
			2	0.0256	0.4272	0.1567	0.0804
Rinsing	009	5/8	1	0.0619	0.4325	0.1587	0.0862
			2	0.0280	0.4330	0.1578	0.0843

Batch Name	Sample No.	Pu Mean Wt % 238	239	240	241	242
Fu2-020	001	2.963	65.829	21.609	6.815	2.785
Fu2-022	003	0.908	66.632	22.529	7.085	2.846
Fu2-033	005	1.515	58.299	25.798	9.374	5.016
Fu2-034	007	1.454	59.042	25.332	9.345	4.828
Rinsing	009	2.585	57.970	25.193	9.251	5.003

Table 13 NMCC Resin Bead
IDM Results for Input
Samples

Batch Name	Sample No.	Date	Measure-ment No	Isotopic Ratio		Concentration	
				U 233/238	Pu 242/239	U (g/l)	Pu (g/l)
Ful-020	001S	5/16	1	0.8686	1.0999	183.0	1.275
			2	0.8663	1.1087	183.4	1.264
	002S	5/29	1	0.8795	1.1055	180.7	1.232
			2	0.8752	1.1064	181.6	1.230
Ful-022	003S	5/20	1	0.8628	1.0856	185.3	1.267
			2	0.8639	1.0841	185.1	1.269
	004S	5/21	1	0.8671	1.0833	184.4	1.270
			2	0.8704	1.0837	183.7	1.269
Ful-033	005S	5/22	1	0.8620	1.1168	184.4	1.458
			2	0.8631	1.1159	184.1	1.460
	006S	5/23	1	0.8665	1.1055	183.4	1.476
			2	0.8609	1.1157	184.6	1.461
Ful-034	007S	5/26	1	0.8789	1.1031	189.4	1.524
			2	0.8796	1.1008	189.3	1.527
	008S	5/26	1	0.8850	1.1038	188.1	1.522
			2	0.8760	1.1013	190.1	1.526
Rinsing	009S	5/27	1	1.7879	2.0284	30.82	0.269
			2	1.7869	2.0042	30.84	0.273
	010S	5/29	1	1.7927	2.0034	30.74	0.267
			2	1.7886	1.9718	30.81	0.272

Table 14

Results of Tracer Measurements - All Labs

U

Lab	Meas.	Date	233/8	234/8	235/8	236/8	233U (at/ml)
PNC	conv.	85-01	484.949	.909	.300	.070	mean 2.7045 E18 RSD .007 % n 5
NMCC	conv.	86-10	497.790	.895	.270	.004	2.7320 E18 n 1
SAL	conv.	86-05	446.030	.824	.278	.064	mean 2.7157 E18 RSD .14 % n 10
SAL	RB	86-03	-	-	-	-	mean 2.6600 E18 RSD .22 % n 8

Pu

Lab	Meas.	Date	238/9	240/9	241/9	242/9	244/9	242Pu (at/ml)
PNC	conv.	85-01*	.02692	1.84572	.92140	58.6968	.0000	mean 1.5303 E16 RSD .018 % n 5
NMCC	conv.	86-10*	.02197	1.83555	.92101	58.2123	.0006	1.5300 E16 n 1
SAL	conv.	86-05*	.02232	1.85969	.90768	58.6119	.0031	mean 1.5336 E16 RSD .30 % n 10
SAL	RB	-	-	-	-	-		mean 1.5531 E16 RSD .27 % n 8

* Measurement date only, all data corrected to 85-01-01

Table 15

Results of Sample Measurements - All Labs

U (g/l)

Sample	PNC-RB	NMCC-RB	SAL-RB		PNC-Conv
			(PNC)	(SAL-RB)	
FU1-020	179.825	182.175	182.320	179.320	180.7
FU1-022	182.325	184.625	185.287	182.238	184.35
FU1-033	182.675	184.125	182.855	179.846	182.8
FU1-034	187.325	189.225	188.338	185.239	189.1
Rinse	30.585	30.75	30.537	30.034	30.70

Pu (g/l)*

Sample	PNC-RB	NMCC-RB	SAL-RB		PNC-Conv
			(PNC)	(SAL-RB)	
FU1-020	1.24425	1.25403	1.22905	1.24736	1.2265
FU1-022	1.25908	1.27262	1.26761	1.28658	1.2665
FU1-033	1.46438	1.46965	1.47660	1.49860	1.457
FU1-034	1.52939	1.53089	1.53030	1.55308	1.5215
Rinse	.26958	.27134	.26683	.27081	.267

* Corrected to 85-07-25

Table 16

Agreement with PNC/TRP Conventional Results

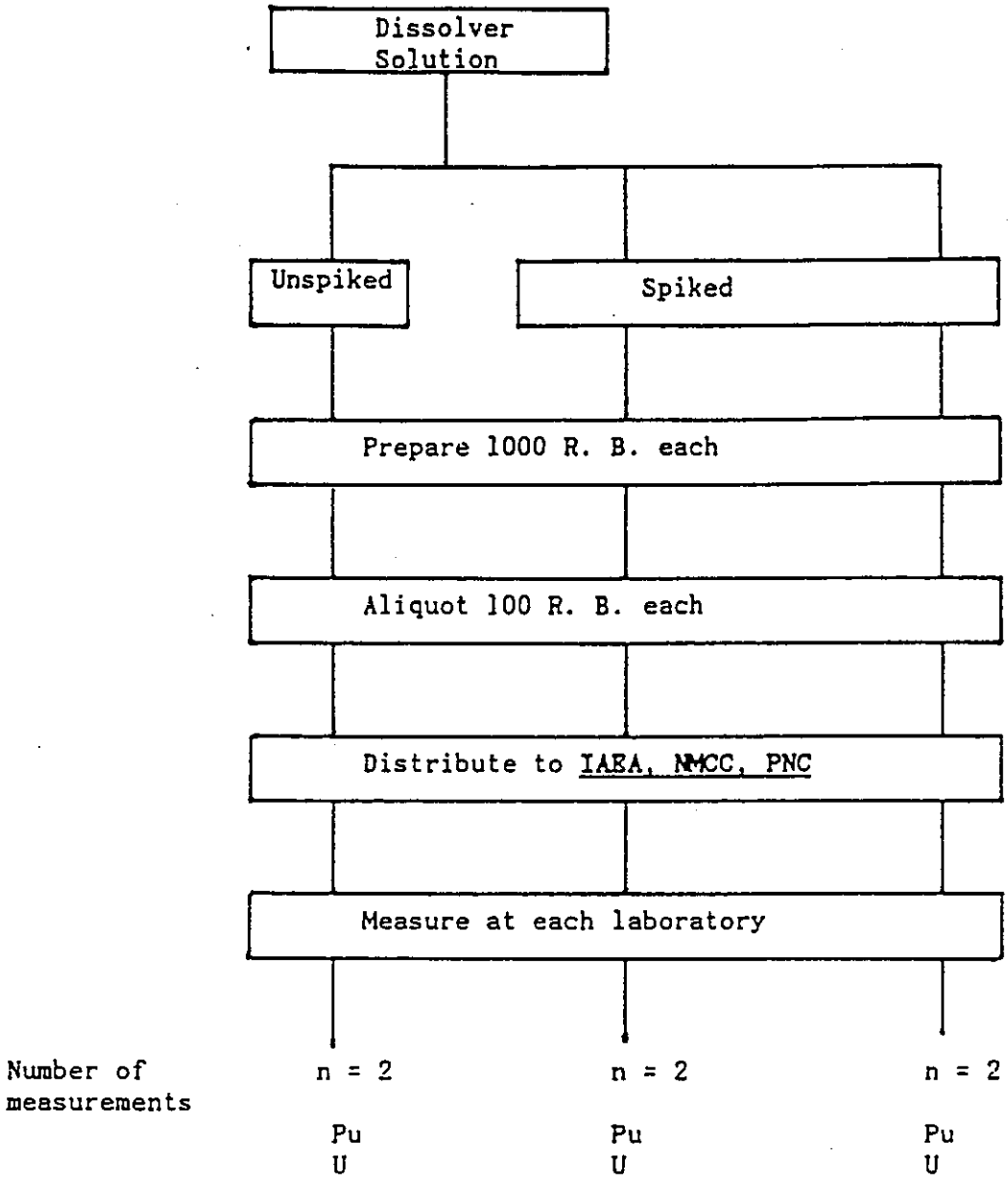
U %

Sample	PNC-RB	NMC-RB	SAL-RB	
			(PNC)	(SAL-RB)
FU1-020	- .48	+ .82	+ .89	- .76
FU1-022	-1.10	+ .15	+ .51	-1.15
FU1-033	- .07	+ .72	+ .03	-1.62
FU1-034	- .94	+ .07	- .40	-2.04
Rinse	- .39	+ .15	- .55	-2.19
mean	- .60	+ .38	+ .10	-1.55
SD	± .42	± .36	± .61	±0.60

Pu (%)

Sample	PNC-RB	NMCC-RB	SAL-RB	
			(PNC)	(SAL-RB)
FU1-020	+1.45	2.24	+ .21	+1.70
FU1-022	- .59	+ .48	+ .09	+1.59
FU1-033	+ .51	+ .87	+1.35	+2.86
FU1-034	+ .52	+ .62	+ .58	+2.08
Rinse	+ .97	+1.63	- .06	+1.43
mean	+.57	+1.17	+.43	+1.93
SD	±.76	± .75	±.56	± .57

Fig. 1 5 batches of 85-1-C



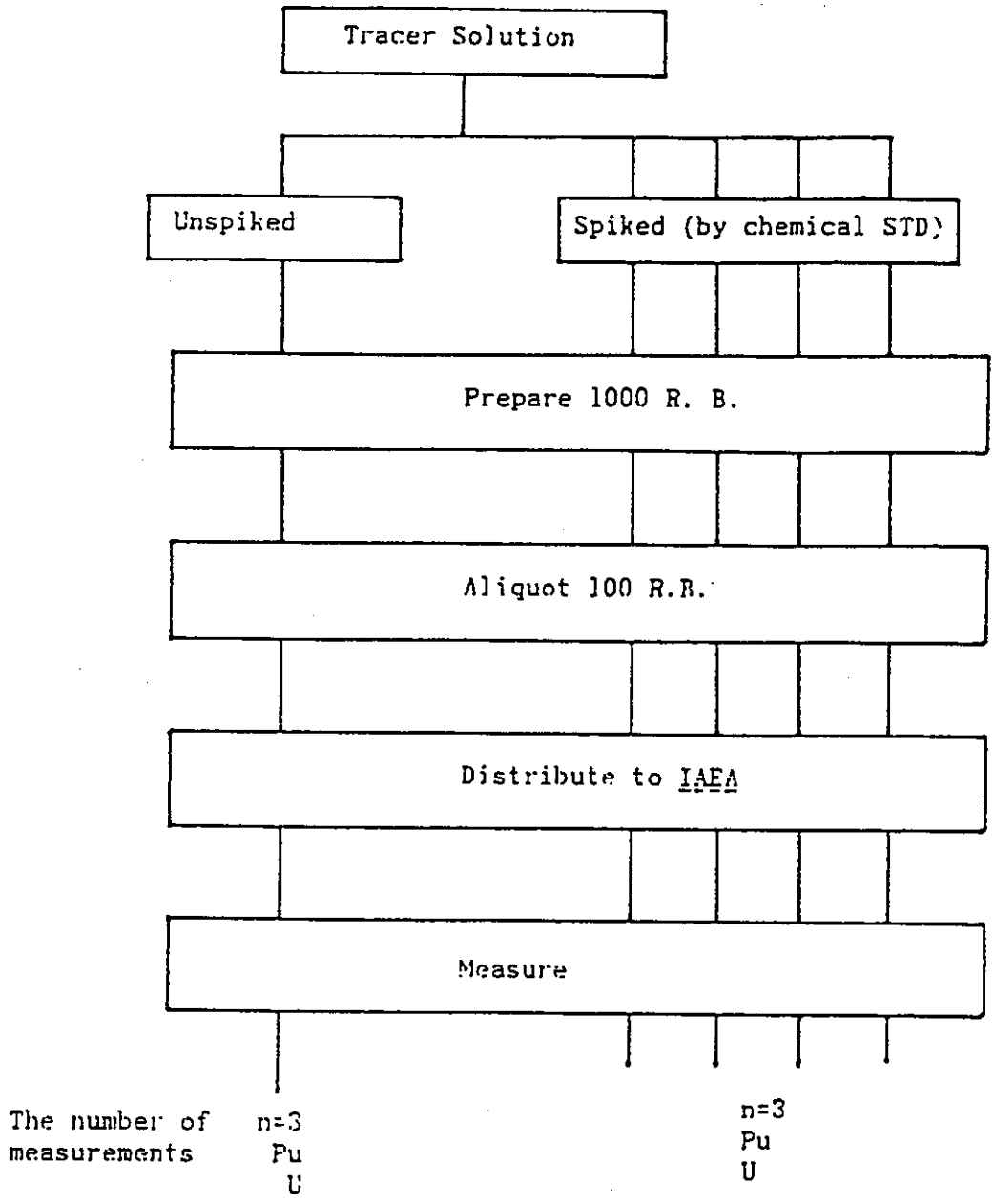


Figure 2: Resin Bead Samples used for correction of mass discrimination effect

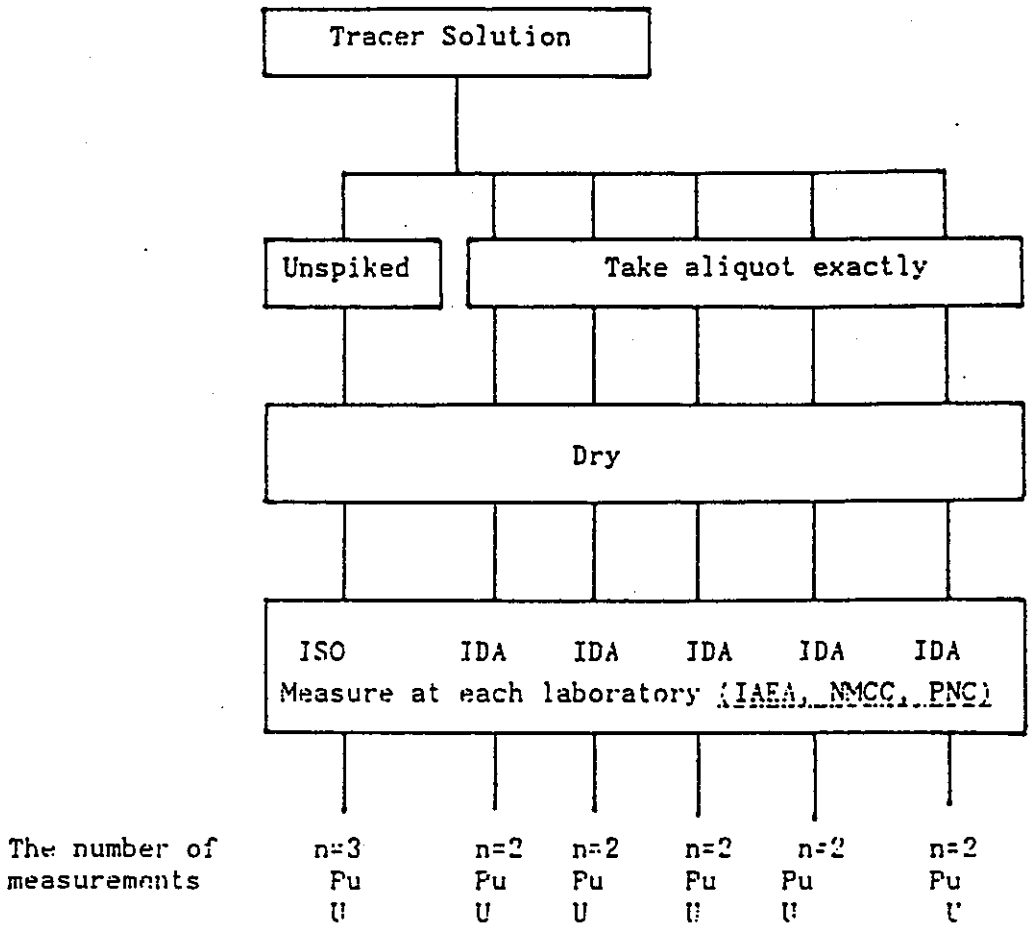


Figure 3: Dried Samples

The list of samples ANNEX A

1. Dissolver Solution (Resin Bead Samples)

	Batch Name	Sample	Bottle No.
1.	Fu2-020	Unspiked	001
		Spiked-1	001S
		Spiked-2	002S
2.	Fu2-022	Unspiked	003
		Spiked-1	003S
		Spiked-2	004S
3.	Fu2-033	Unspiked	005
		Spiked-1	005S
		Spiked-2	006S
4.	Fu2-034	Unspiked	007
		Spiked-1	007S
		Spiked-2	008S
5.	1st-Rinsing	Unspiked	009
		Spiked-1	009S
		Spiked-2	010S

2. Tracer Solution (Dried Samples)

1. For IDM : T001 T005

2. For Isotopic Composition : T006

3. Tracer Solution (Resin Bead Samples)

1. Spiked (Tracer + Standard) : M001 M004

2. Unspiked (Tracer) : RT01 RT02

JASPAS JC-4 SIXTH TAEA-NMCC PNC PESIN BEAD EXPERIMENT

ANNEX 2 PNC - TRP DATA ON THE DLLUTION AND SPHKING OF THE SAMPLES

Bottle No.	Sample Name	Preparation Data	1 st Sampling	Diluted Volume (m1)	Diluted Volume (m1)	2nd Sampling Factor	Tracer Volume (m1)
001	Fu-2-020 Unspiked	18.07.85	1.0251	149.89	147.22	2.0507	
001S	Spiked-1					2.0507	2.0449
002S	Spiked-2					2.0507	2.0449
003	Fu-2-002 Unspiked	19.07.85	1.0282	149.89	146.78	2.0382	
003S	Spiked-1					2.0382	2.0513
004S	Spiked-2					2.0382	2.0513
005	Fu-2-033 Unspiked	25.07.85	1.0093	149.89	149.51	2.0774	
005S	Spiked-1					2.0774	2.0464
006S	Spiked-2					2.0774	2.0464
007	Fu-2-034 Unspiked	26.07.85	1.0064	149.89	149.94	2.0043	
007S	Spiked-1					2.0043	2.0623
008S	Spiked-2					2.0043	2.0623
009	1st-Rinsing-Un-Spiked	30.07.85	1.0306	49.96	49.48	1.9858	
009S	Spiked-1					1.9858	2.0537
010S	Spiked-2					1.9858	2.0537

$$\text{Dilution factor} = \frac{\text{1st Sampling (ml)} + \text{Diluted Volume (ml)}}{\text{1st Sampling (ml)}}$$

JASPAS JC-4 SIXTH IAEA-NMCC-PNC RESIN BEAD EXPERIMENT

ANNEX 3 PNC-TRP DATA ON MIXED TRACER (Dried Samples)

1. Bottle No. : T001 T006
2. Sampling Volume of Mixed tracer (ml/Bottle) : 1.0238 ml
3. Approximate Concentration :

U-233 2.7 E + 18 atoms/ml

Pu-243 1.5E + 16 atoms /ml

JASPAS JC-4 Sixth IAEA-NMCC-PNC RESIN BEAD EXPERIMENT

ANNEX 4 PNC-TRP DATA ON THE MIXED STANDARD (MEASUREMENT DATE: 25 FEB.85)

1. Concentration of U and Pu atoms in mixed standard solution

U-238 2.9019 x 10 E + 18 (atoms / ml)

Pu-239 1.4993 x 10 E + 16 (atoms / ml)

2. Isotopic abandance of U and Pu atoms in mixed standard solution

1) Uranium

Ratio		Atom %	
R 58	0.007264	U-234	0.00535
R 45	0.007413	U-235	0.7211
R 65	--------	U-236	-------
		U-238	99.2737

2. Plutonium

Ratio		Atom %	
R 89	0.000098	Pu-238	0.0095
R 09	0.029007	Pu-239	97.1177
R 19	0.000524	Pu-240	2.8151
R 29	0.000050	Pu-241	0.0508
		Pu-242	0.0049

3. Preparation of resin bead (Mixed tracer + Mixed standard)

1. Date: 06 Sept. 85

2. Volume of tracer and standard solution

1) Mixed tracer: 2.0524 ml

2) Mixed standard : 2.0265 ml

88-02285

JASPAS Programme Task JC-4

Isotopic and Isotope Dilution Analysis of Spent Fuel Solution by Resin Bead Mass Spectrometry

Result of the Seventh Interlaboratory Experiment

T.Akiyama, S.Terakado, Y.Kuno, M.kamata, K.kaminaga

K.Abe, PNC/TRP Tokai-mura, Japan

S.Deron, R.Fiedler, SAL/IAEA, Seibersdorf

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1. Introduction

Upon analysing uranium and plutonium contained in the feed-accounting tank solution, the resin bead technique is provided with several advantages over the conventional methodes in both transport and measurement. This is because the sample prepared by the resin bead technique is considered to be mailable due to the extremely small amount of nuclear material, and because uranium and plutonium can be measured simultaneously.

To identify the effectiveness of the resin bead technique, it had been developed as the TASTEX Task-J from 1979, and has been developed as the JASPAS (Japan's Supporting Program for Agency's Safeguards) Task-JC 4 since 1982. The joint experiments have been held six times, so far. As the results of the three partite (the PNC/IAEA-SAL/NMCC) joint analysis (See the report of the 6th joint experiment) indicated, the resin bead technique was well

qualified for safeguards analysis.

If the resin bead technique is to be used routinely, however, a great number of samples must be treated hereafter, and thereby the radiation exposure of operators due to this operation will increase. To solve this problem, a glove box line exclusive for treating resin beads was installed, and an automatic resin bead treatment system (robotic resin bead treatment system) was designed and manufactured.

The 7 the joint experiment was performed to verify the performance of this automatic resin bead treatment system, confirming that the system worked well and was free from the effect of contamination.

2. Design of Experiment and Preparation of the Samples

The design and development of the robot for resin bead treatment were completed in 1986, and it was installed in the glove box line exclusive for resin bead treatment after a series of cold performance tests. Using this robotic resin bead treatment system, 10-batch samples taken from the 88-1 reprocessing campaign were treated.

A spent-fuel-dissolved solution was accurately diluted (dilution ratio 150 times) and aliquots were prepared, followed by the addition and mixing of the spike (233U-242Pu mixed spike) prepared by the PNC. The composition of the mixed spike is shown in Table, whereas the amounts of the samples and spike in Table. After valency adjustment by using Fe^{2+} and $NaNO_2$, the mixed solution was subjected to adsorption by resin beads and then to washing of them for the removal of FPs. The resin bead sample thus prepared was packed into the A-type container for air transport and shipped to the IAEA-SAL.

3. Results and Discussions

The resin beads were measured jointly be the IAEA-SAL and the ORNL. Since the key objective of the PNC of this time was to conduct the performance tests of the robot for resin bead treatment, the PNC performed measurement only by the conventional method (measurement by the thermoionic mass spectrometer after the application of solution to the sample). The composition of the spiked solution after adjusting the resin beads and the data of taking the samples and spiked solutions are shown in Annexes 1 and 2, respectively.

3-1 Conventional Measurement Method for Samples

The conventional measurement method (measurement by the thermoionic mass spectrometer after the application of solution to the sample) was adopted in the PNC and the IAEA-SAL for measurement. The results are given in Annex 3 and Table 1 (Table 1 includes the results of measurement obtained by the resin bead technique carried out in the ORNL).

3-2 Comparison of Data Obtained by Three Parties

Table 1 shows the results measured by the resin bead technique in the ORNL and those by the conventional technique (measurement by the thermoionic mass spectrometer after the application of solution to the sample) in both the IAEA-SAL and the PNC. Although the results obtained by the three parties were well coincided with each other as a whole, slight differences were observed in plutonium concentrations (ORNL-IAEA/SAL: 1.25%, PNC/TRP-IAEA/SAL: 0.81%) as compared with uranium concentrations. This may stem from different spiked solutions used by the IAEA-SAL, the ORNL and the PNC. The resin bead samples, on the other hand, were prepared by the PNC using the same spike, so the results

obtained by the ORNL and the PNC were well coincided with each other, showing that the accuracy of the resin bead technique itself is as good as those in the previous six experiments. The error originated from the difference in spiking solutions is considered to be eliminated by using large-size dried (LSD) spikes (to be used jointly by the PNC, the IAEA-SAL and the NMCC) which will be put into practical use, soon.

4. Conclusions

The results of the 7th experiment, like the previous 6 experiments, confirmed that the accuracy of the resin bead technique was the same as that of the conventional sample-application method. This fact shows that the robot for resin bead treatment works well and gives no adverse effect such as contamination at the time of resin bead preparation. Consequently, sample treatment was simplified and the applicability to safeguards samples become wide.

JASPAS - JC-4 -SEVENTH PNC-IAEA RESIN BEAD EXPERIMENT

ANNEX 1- PNC-TRP DATA ON THE MIXED TRACER

The measurement result of mixed tracer sample

(measurement date 88.01.11~88.01.13)

1. Concentration of U and Pu atoms in mixed tracer solution.

U -233	2.9213×10E+18 (atoms/ml)
Pu-242	1.5806×10E+16 (atoms/ml)

2. Result of isotopic measurement

1) U-233

Ratio		Atom%	
R38	348.831	233	99.460
R48	0.6000	234	0.1711
R58	0.2334	235	0.0666
R69	0.0572	236	0.0163
		238	0.2851

2) Pu-242

Ratio		Atom%	
R89	0.04336	238	0.0149
R09	4.56813	239	0.3433
R19	0.21777	240	1.5678
R29	285.7425	241	0.0747
		242	97.9993

JASPAS-JC-4 SEVENTH IAEA-NMCC-PNC RESIN BEAD EXPERIMENT

ANNEX 2 PNC-TRP DATA ON THE DILUTION AND SPIKING OF SAMPLES

Bottle No.	Sample Name	Preparation Date	1st Sampling Volume (mℓ)	Diluted Volume (mℓ)	Dilution Factor	2nd Sampling Volume (mℓ)	Tracer Volume (mℓ)
	MI1−094−Unspiked	16.02.88	1.0040	149.82	150.22	2.0149	———
	Spiked					2.0149	2.0034
	MI1−095−Unspiked	17.02.88	1.0041	149.82	150.21	2.0188	———
	Spiked					2.0188	2.0039
	MI1−096−Unspiked	18.02.88	1.0002	149.82	150.79	1.9945	———
	Spiked					1.9945	1.9955
	MI1−097−Unspiked	19.02.88	1.0100	149.82	149.34	2.0192	———
	Spiked					2.0192	1.9986
	MI1−098−Unspiked	19.02.88	1.0004	149.82	150.76	2.0140	———
	Spiked					2.0140	2.0110

$$\text{Dilution Factor} = \frac{\text{1st Sampling (mℓ)} + \text{Diluted Volume (mℓ)}}{\text{1st Sampling (mℓ)}}$$

JASPAS-JC-4 SEVENTH IAEA-NMCC-PNC RESIN BEAD EXPERIMENT

ANNEX 2 PNC-TRP DATA ON THE DILUTION AND SPIKING OF SAMPLES

Bottle No.	Sample Name	Preparation Date	1st Sampling Volume (mℓ)	Diluted Volume (mℓ)	Dilution Factor	2nd Sampling Volume (mℓ)	Tracer Volume (mℓ)
	MI1-099 – Unspiked	20.02.88	1.0114	149.82	149.13	2.0100	———
	Spiked					2.0100	2.0119
	MI1-100 – Unspiked	21.02.88	1.0045	149.82	150.15	2.0030	———
	Spiked					2.0030	1.9993
	MI1-101 – Unspiked	22.02.88	1.0043	149.82	150.18	1.9944	———
	Spiked					2.0072	1.9929
	MI1-102 – Unspiked	23.02.88	0.9975	149.82	151.20	2.0073	———
	Spiked					2.0073	2.0105
	MI1-103 – Unspiked	24.02.88	0.9993	149.82	150.92	2.0098	———
	Spiked					2.0098	2.0058

$$\text{Dilution Factor} = \frac{\text{1st Sampling (mℓ)} + \text{Diluted Volume (mℓ)}}{\text{1st Sampling (mℓ)}}$$

JASPAS-JC-4 SEVENTH IAEA-NMCC-PNC RESIN BEAD EXPERIMENT

ANNEX 3 ISOTOPIC AND ISOTOPE DILUTION ANALYTICAL RESULTS OF PNC (U)

		MI1-094	MI1-095	MI1-096	MI1-097	MI1-098
Unspiked Sample	Preparation date	16.02.88	17.02.88	18.02.88	19.02.88	19.02.88
	U Ratio R48 R58 R68	 0.000144 0.009832 0.002501	 0.000144 0.009439 0.002480	 0.000134 0.009232 0.002449	 0.000134 0.009190 0.002428	 0.000144 0.009686 0.002358
	U Atom% 234 235 236 238	 0.014 0.971 0.247 98.768	 0.014 0.933 0.245 98.808	 0.013 0.912 0.242 98.833	 0.013 0.908 0.240 98.839	 0.014 0.957 0.233 98.796
	U Weight% 234 235 236 238	 0.014 0.959 0.245 98.782	 0.014 0.921 0.243 98.822	 0.013 0.901 0.240 98.846	 0.013 0.897 0.238 98.852	 0.014 0.945 0.231 98.810
Spiked Sample	U R(83)M −1 −2	 1.047084 1.043779	 0.953841 0.951512	 0.978363 0.982525	 1.064522 1.063718	 0.963020 0.964557
	U (Conc. g/ℓ) −1 −2	 182.3 181.8	 165.7 165.3	 171.9 172.7	 183.3 183.2	 168.9 169.2

JASPAS-JC-4 SEVENTH IAEA-NMCC-PNC RESIN BEAD EXPERIMENT

ANNEX 3 ISOTOPIC AND ISOTOPE DILUTION ANALYTICAL RESULTS OF PNC (U)

		MII-099	MII-100	MII-101	MII-102	MII-103
	Preparation date	20.02.88	21.02.88	22.02.88	23.02.88	24.02.88
Unspiked Sample	U Ratio R48 R58 R68	 0.000144 0.009924 0.003248	 0.000216 0.010370 0.002298	 0.000144 0.010110 0.002297	 0.000144 0.009655 0.002358	 0.000144 0.009676 0.002327
	U Atom% 234 235 236 238	 0.014 0.979 0.321 98.686	 0.021 1.024 0.227 98.728	 0.014 0.999 0.227 98.760	 0.014 0.954 0.233 98.799	 0.014 0.956 0.230 98.800
	U Weight% 234 235 236 238	 0.014 0.968 0.230 98.788	 0.021 1.011 0.225 98.743	 0.014 0.986 0.225 98.775	 0.014 0.942 0.231 98.813	 0.014 0.944 0.228 98.814
Spiked Sample	U R(83)M −1 −2	 0.947248 0.947438	 1.031339 1.032208	 0.890870 0.890691	 0.866179 0.862790	 0.820314 0.819946
	U (Conc. g/ℓ) −1 −2	 164.8 164.8	 180.3 180.4	 154.8 154.8	 151.5 150.9	 143.9 143.8

JASPAS-JC-4 SEVENTH IAEA-NMCC-PNC RESIN BEAD EXPERIMENT

ANNEX 3 ISOTOPIC AND ISOTOPE DILUTION ANALYTICAL RESULTS OF PNC (Pu)

		M I 1 − 0 9 4	M I 1 − 0 9 5	M I 1 − 0 9 6	M I 1 − 0 9 7	M I 1 − 0 9 8
Unspiked Sample	Preparation date	16.02.88	17.02.88	18.02.88	19.02.88	19.02.88
	Pu Ratio					
	R 8 9	0.011809	0.010810	0.011613	0.011143	0.010001
	R 0 9	0.338431	0.343772	0.347353	0.346508	0.334114
	R 1 9	0.155562	0.158176	0.159242	0.159194	0.152083
	R 2 9	0.046376	0.048567	0.049623	0.049290	0.044680
	Pu Atom%					
	2 3 8	0.761	0.692	0.741	0.711	0.649
	2 3 9	64.426	64.048	63.782	63.851	64.898
	2 4 0	21.804	22.018	22.155	22.125	21.683
	2 4 1	10.022	10.131	10.157	10.165	9.870
	2 4 2	2.987	3.111	3.165	3.147	2.900
	Pu Weight%					
	2 3 8	0.756	0.688	0.736	0.707	0.645
	2 3 9	64.291	63.912	63.646	63.715	64.764
	2 4 0	21.849	22.063	22.200	22.170	21.729
	2 4 1	10.085	10.194	10.220	10.228	9.932
	2 4 2	3.019	3.143	3.198	3.180	2.930
Spiked Sample	Pu R (92) M − 1	0.861855	0.785900	0.796883	0.870224	0.777784
	− 2	0.862765	0.784385	0.796153	0.869552	0.778432
	Pu (Conc. g／ℓ) − 1	1.303	1.191	1.229	1.318	1.170
	− 2	1.305	1.188	1.227	1.317	1.171

JASPAS-JC-4 SEVENTH IAEA-NMCC-PNC RESIN BEAD EXPERIMENT

ANNEX 3 ISOTOPIC AND ISOTOPE DILUTION ANALYTICAL RESULTS OF PNC (Pu)

		M I I − 0 9 9	M I I − 1 0 0	M I I − 1 0 1	M I I − 1 0 2	M I I − 1 0 3
Unspiked Sample	Preparation date	20.02.88	21.02.88	22.02.88	23.02.88	24.02.88
	Pu Ratio					
	R 8 9	0.009950	0.008300	0.009892	0.010437	0.009732
	R 0 9	0.329533	0.322600	0.323876	0.335048	0.332457
	R 1 9	0.148626	0.145629	0.145465	0.151420	0.149893
	R 2 9	0.042611	0.039824	0.040129	0.044245	0.043023
	Pu Atom%					
	2 3 8	0.650	0.547	0.651	0.677	0.634
	2 3 9	65.328	65.947	65.817	64.887	65.142
	2 4 0	21.528	21.276	21.317	21.740	21.657
	2 4 1	9.710	9.604	9.574	9.825	9.764
	2 4 2	2.784	2.626	2.641	2.871	2.803
	Pu Weight%					
	2 3 8	0.646	0.544	0.647	0.673	0.630
	2 3 9	65.196	65.816	65.686	64.753	65.009
	2 4 0	21.574	21.321	21.363	21.786	21.703
	2 4 1	9.771	9.665	9.635	9.887	9.826
	2 4 2	2.813	2.654	2.669	2.901	2.832
Spiked Sample	Pu R (9 2) M − 1	0.763409	0.835230	0.718528	0.701538	0.654279
	− 2	0.765040	0.834611	0.717594	0.701905	0.653832
	Pu (Conc. g / ℓ) − 1	1.128	1.222	1.049	1.048	0.974
	− 2	1.131	1.221	1.047	1.049	0.973

Table 1

Results of Seventh Resin Bead Experiment
Valid for 1988-03-01

LAB	BATCH	^{234}U	^{235}U	^{236}U	^{238}U	^{238}Pu	^{239}Pu	^{240}Pu	^{241}Pu	^{242}Pu	U, g/l	Pu, g/l
ORNL/RB	94	.016	.960	.246	98.779	.769	64.296	21.838	10.068	3.029	181.69	1.307
SAL		.013	.951	.243	98.793	.750	64.276	21.859	10.085	3.030	182.09	1.294
TRP		.014	.959	.245	98.782	.756	64.291	21.849	10.085	3.019	182.00	1.304
ORNL/RB	95	.015	.923	.244	98.818	.782	63.932	22.056	10.127	3.103	165.78	1.187
SAL		.013	.918	.240	98.829	.745	63.910	22.100	10.133	3.112	164.92	1.178
TRP		.014	.921	.243	98.822	.688	63.912	22.063	10.194	3.143	165.50	1.189
ORNL/RB	96	.016	.902	.241	98.841	.791	63.658	22.186	10.192	3.172	172.09	1.232
SAL		.013	.898	.239	98.850	.755	63.639	22.189	10.223	3.193	172.29	1.223
TRP		.013	.901	.240	98.846	.736	63.646	22.200	10.220	3.198	172.30	1.228
ORNL/RB	97	.015	.901	.240	98.843	.787	63.703	22.156	10.179	3.174	182.57	1.322
SAL		.015	.902	.240	98.841	.798	63.643	22.159	10.220	3.180	183.35	1.309
TRP		.013	.897	.238	98.852	.707	63.715	22.170	10.228	3.180	183.20	1.318
ORNL/RB	98	.014	.946	.232	98.808	.726	64.591	21.785	9.946	2.951	167.89	1.179
SAL		.017	.946	.232	98.801	.728	64.683	21.737	9.924	2.929	168.20	1.158
TRP		.014	.945	.231	98.810	.645	64.764	21.729	9.932	2.930	169.00	1.170
ORNL/RB	99	.014	.970	.231	98.784	.683	65.190	21.578	9.746	2.803	163.51	1.131
SAL		.014	.968	.230	98.787	.697	65.177	21.553	9.769	2.804	164.72	1.119
TRP		.014	.968	.230	98.788	.646	65.196	21.574	9.771	2.813	164.80	1.130
ORNL/RB	100	.015	1.008	.225	98.751	.661	65.770	21.279	9.634	2.656	178.73	1.235
SAL		.013	1.003	.224	98.760	.673	65.735	21.274	9.659	2.659	178.89	1.220
TRP		.021	1.011	.225	98.743	.544	65.816	21.321	9.665	2.654	180.30	1.222
ORNL/RB	101	.014	.979	.228	98.779	.657	65.737	21.340	9.604	2.661	155.69	1.060
SAL		.013	.974	.226	98.787	.664	65.700	21.343	9.633	2.660	155.86	1.055
TRP		.014	.986	.225	98.775	.647	65.686	21.363	9.635	2.669	154.80	1.048

Table 1 (cont'd)

ORNL/RB	102	.015	.943	.232	98.810	.712	64.844	21.729	9.842	2.873	147.70	1.036
SAL		.013	.937	.230	98.820	.672	64.777	21.787	9.809	2.875	148.34	1.020
TRP		.014	.942	.231	98.813	.673	64.753	21.786	9.887	2.901	151.20	1.049
ORNL/RB	103	.014	.949	.229	98.808	.686	65.085	21.643	9.769	2.810	142.06	.983
SAL		.013	.941	.226	98.820	.690	65.027	21.660	9.803	2.819	142.84	.964
TRP		.014	.944	.228	98.814	.630	65.009	21.703	9.826	2.832	143.90	.973
100*(ORNL-SAL)/SAL	%d±RSD	9.0 ±12	0.45 ±.34	.77 ±.55	-.007 ±.007	1.1 ±3.1	.037 ±.070	-.032 ±.14	-0.23 ±.20	-0.063 ±.35	-0.23 ±0.34	1.25 ±.53
100*(ORNL-TRP)/TRP		3.8 ±14	0.11 ±.41	.51 ±.35	-.003 ±.006	9.0 ±6.0	.003 ±.11	-.077 ±.15	-0.34 ±.23	-0.33 ±.60	-0.58 ±0.81	0.44 ±.75
100*(TRP-SAL)/SAL		6.9 ±21	0.37 ±.52	.26 ±.67	-.003 ±.011	-7.0 ±6.2	.034 ±.063	.046 ±.12	0.10 ±.19	0.27 ±.44	0.35 ±0.70	0.81 ±.88

CONCLUSION

Since the investigation on the resin bead sampling and measurement thecnique started in 1979 as the TASTEX-Task J, it has been energetically developed, including the joint experiments carried out seven times.

The resin bead measurement technique and its accuracy, owing to the developmental efforts and the joint experiments, have made remarkable progress as compared with the initial stage of development, and become comparable to those of the conventional method. The resin bead technique, as pointed out in the IAEA report, enables uranium and plutonium to be simultaneously measured without separating them, resulting in the advantage of simplified measurement; however, the measurement technique requires far higher proficiency in comparison with the conventional method.

As to the preparation of the resin beads, the improvement of sample preparation process, installation of the glove box line exclusive for the robotic resin bead treatment system and the development of the robot for automating the system could mostly eliminate the contamination problem etc. occurring frequently in the initial stage of development. However, part of the resin bead technique still remains to be automated, and requires high technical proficiency like in measurement. Therefore, if resin bead sampling is to be performed routinely as inspection analysis, it should be further improved in this sense. Meanwhile, in the joint experiments the newly installed equipment and improved operators' skills helped eliminate mostly the contamination problem, but if resin bead sampling is carried out routinely, problems associated with the contamination of the equipment and/or dispersion in the proficiency of operators might arise.

The most outstanding advantage of the resin bead technique is that since the sample is resin beads adsorbing the trace amounts of uranium and

plutonium and does not contain fission products, it presumably does not need any special transport container and could be treated as an ordinary mail. According to the opinion of Japan Ministry of Posts and Telecommunications in this regard, however, treatment as a mail is very difficult because of many problems in putting this idea into practical use.

As to technical development of feed-accounting inspection analysis, the Richmann's densitometry and the γ-spectrometry for resin bead samples have been caried out as part of the JASPAS and as the technical cooperation project between the PNC and the DOE, respectively. In particular, the Richmann's densitometry is going to be used for inspection analysis in the near future, so the timeliness of inspection analysis for the feed-accounting samples can be ensured. In addition, part of the results of investigation and development we have obtained hitherto has been effectively used in the γ-spectrometry for the resin bead samples.

As mentioned above, although much knowledge was obtained on the sampling technique from the feed-accounting tank by neans of the resin bead technique together with the measurement technique by using it and although some fruitful results were thereby obtained, we had to draw conclusion that the application of the resin bead technique to the actual inspection is difficult because of the difficulties of applying the method to routine analysis and of mailing the samples. Therefore, the development of the resin bead technique is decided to be suspended.

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