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A $^{233}U/^{236}U/^{242}Pu/^{244}Pu$ spike for Isotopic and Isotope Dilutior Analysis by Mass Spectrometry with Internal Calibration

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30 63 05 94 00 94 45 48 57 61 43 67 18 25 75 92 95 67

Abstract

The Khlopin Radium Institute prepared on behalf of the IAEA a synthetic mixture of ^{233}U, ^{236}U, ^{242}Pu and ^{244}Pu isotopes. The isotopic composition and elemental concentration of uranium and plutonium were certified on the basis of analyses done by four laboratories of the IAEA Network, using mass spectrometry with internal standardization. The certified values for $^{233}U/^{236}U$ ratio and the ^{236}U chemical concentration have a coefficient of variation of 0.05%. The latter is fixed by the uncertainty in the $^{235}U/^{238}U$ ratio of NBS500 used as internal standard. The coefficients of variation of the $^{244}Pu/^{242}Pu$ ratio and the ^{242}Pu chemical concentration are respectively 0.10% and 0.16% and limited by the uncertainty in the $^{240}Pu/^{239}Pu$ ratio of NBS947.

This four isotope mixture was used as an internal standard as well as a spike, to analyze 30 batches of LWR spent fuel solutions. The repeatability of the mass spectrometric measurements have a coefficient of variation of 0.025% for the uranium concentration, and of 0.039% for the plutonium concentration. The spiking and treatment errors had a coefficient of variation of 0.048%.

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1. Introduction

The precision and accuracy of isotopic and isotope dilution analyses of uranium and plutonium can be improved by a factor 3-10 by the use of internal standards (1, 2). The International Atomic Energy Agency (IAEA), analyzes in this way since 1985 a good fraction of the samples taken by its safeguards inspectors at spent fuel reprocessing plants for the verification of the accountability of the input solutions.

The batch of spike now in use is referenced SAL-9914 /QS87 and was prepared by the Khlopin Radium Institute (RI) (3). It is certified on the basis of analyses performed by four laboratories of the IAEA Network.

This report presents the results of the certification measurements and gives an example of the precision achieved in the isotope dilution analyses of Safeguards inspection samples.

2. Preparation of the SAL-9914 (QS 87) Spike

The QS 87 spike was prepared at KRI as follows.

A mixture of uranium isotopes was obtained by mixing known quantities of the Soviet Certified Reference Material FCO 3213-85 containing 97.20% enriched ^{233}U and a 99.97% enriched ^{236}U also of Soviet origin. It was verified by alpha spectrometry that this mixture was free from plutonium ($Pu/U << 10^{-6}$)

A solution of plutonium isotope was prepared separately by dissolving a unit of the Certified Reference Material NBS-996 containing 97.87% enriched ^{244}Pu with a solution of the Working Reference Material CO-009-87 of RI, prepared from 94.65% enriched ^{242}Pu. A redox cycle was carried out with hydrazine and nitric acid before purification by anion exchange chromatography with a VP-1 resin, and a 95% recovery yield. The U/Pu mass ratio in the purified solution was measured by laser fluorimetry and found to be equal to 1.9×10^{-5}.

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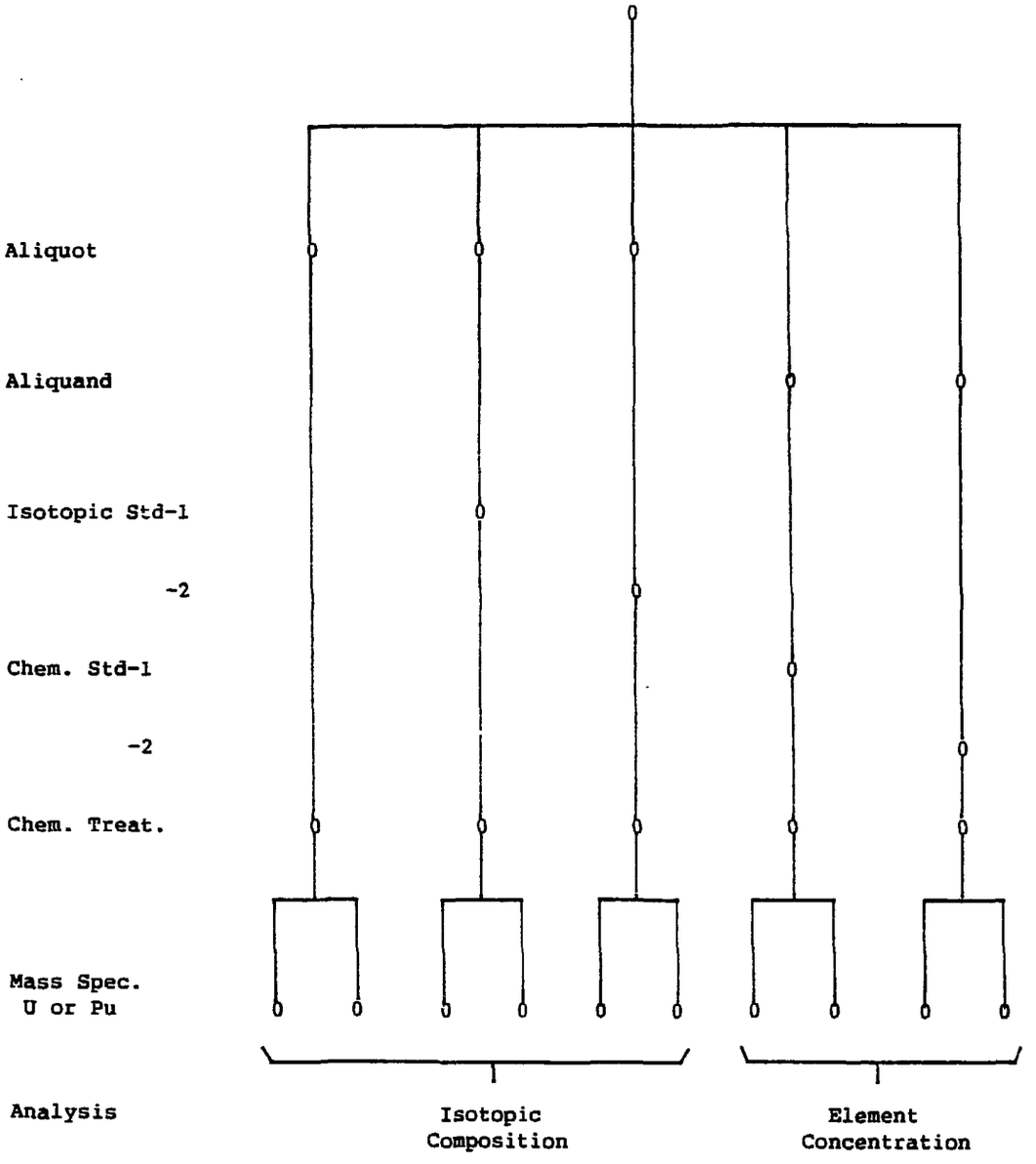

Figure 1: Scheme of analysis of the characterization of QS 87

Samples of the uranium and plutonium mixtures were analyzed at three IAEA Network Laboratories. The results being in good agreement, RI weighed the two feed solutions, mixed them together, and added an aliquand of nitric acid to obtain 2 liters of a solution of the four isotopes in 7 M HNO_3.

The recorded weights and the isotope dilution mass spectrometric analyses of the uranium and plutonium feed mixtures by RI were used to calculate the expected content of the final solution (^{236}U = 504.49 /ug/g, ^{242}Pu = 4.5281/ug/g).

The stock solution was finally divided into 20 aliquots of about 100 ml which were sealed into glass ampoules.

Details of the preparation are described in Annex 3 (3).

3. Characterization Measurements

The certification of the QS 87 spike is based on isotopic and isotope dilution analyses of the final mixture of four isotopes at four laboratories: the Radium Institute in Leningrad (RI), the Centre d'Etudes Nucléaires de Saclay (CENS), the Bundesanstalt fuer Materialpruefung (BAM) in Berlin, and the Safeguards Analytical Laboratory of the IAEA (SAL). Each laboratory received three samples taken at the time of the filling of the first, tenth and twentieth ampoule.

The mass spectrometric measurements were all done with internal standard normalization using a Varian TH5 at RI, a VG354 at CENS, a multidetector MAT-261 at BAM and SAL.

Each laboratory analyzed the isotopic composition of the uranium and plutonium in two (or three) samples according to a scheme similar to the one shown on Figure 1. One or two subsamples of each analyzed sample was spiked with a solution of NBS-U-500 or NBS-Pu-947 isotopic reference material prepared at the laboratory. RI performed in addition a set of uranium isotopic analyses using the soviet isotopic standard FCO-2702-83 ($^{235}U/^{238}U$=1) and FCO-2704-83 ($^{235}U/^{238}U$=10).

Each laboratory determined the concentration of the uranium and plutonium in three (or two) samples according to the scheme shown on Figure 1. One (or two) aliquand(s) of each analyzed sample was (were) spiked with an aliquand of a chemical standard solution prepared at the laboratory. The standard solutions for the isotope dilution assay of uranium were prepared from NBS 960 (RI, BAM, SAL) or MU1 (CENS) certified reference materials. Standard solutions of NBS-949 (RI, SAL) and MP1/EC 201 (CENS, BAM) were used as spikes for the isotope dilution assay of plutonium. RI and BAM used separate uranium and plutonium chemical standard solutions as spikes. SAL and CENS used mixed uranium and plutonium spikes.

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Table 1: Results of Isotopic Analysis;
Isotope Ratios valid for 1989-06-01 (x100)

LAB	SAMPLE	UNSPIKED		STD	SPIKED		233/236 or 238/242	234/236 or 239/242	235/236 or 240/242	238/236 or 241/242	244/242
		ALIQ	FIL		ALIQ	FIL					
SAL	01	1	1	1	1	1	101.687	2.7750	.09747	.07826	
			2			2	101.682	2.7748	.09722	.07998	
	20	1	1	1	1	1	101.689	2.7755	.09681	.07866	
			2			2	101.648	2.7761	.09615	.07983	
LEN	00	1	1	2	1	1	101.756	2.7819	.09601	.07818	
		1	1	3	1	1	101.789	2.7825	.09602	.07817	
	01	1	1	1	1	1	101.769	2.7798	.09690		
			1			2	101.765	2.7785	.09668		
	10	1	1	1	1	1	101.751	2.7809	.09682	.07993	
			1			2	101.759	2.7741	.09624	.07931	
SAC	01	1	1	1	1	1	101.727	2.7809	.10010	.08730	
			1		2	1	101.767	2.7816	.10010	.08730	
	20	1	1	1	1	1	101.722	2.7734	.09810	.07830	
			1		2	1	101.799	2.7748	.09810	.07830	
BAM	01	1	1	1	1	1	101.699	2.7732	.09138	.08634	
			2			2	101.767	2.7762	.09555	.06244	
	10	1	1	1	1	1	101.786	2.7753	.09262	.08487	
			2			2	101.746	2.7754	.09314	.07094	
	20	1	1	1	1	1	101.741	2.7735	.09152	.08586	
			2			2	101.762	2.7757	.09283	.06916	
SAL	01	1	1	1	1	1	0.10096	.04922	4.5197	.1763	39.037
			2			2	0.10105	,04979	4.5206	.1759	39.039
	20	1	1	1	1	1	0.10327	.05091	4.5175	.1693	39.040
			2			2	0.10314	.04932	4.5194	.1746	39.057
Len	01	1	1	1	1	1	0.10243		4.5282	.1764	39.034
			1			2	0.10259		4.5220	.1713	39.015
	1^	1	1	1	1	1	0.10235	.06384	4.5172	.1754	39.026
			1			2	0.10269	.06400	4.5171	.1761	39.006
SAC	01	1	1	1	1	1	0.09997	.05120	4.5156	.1726	39.044
			1		2	1	0.09978	.05130	4.5188	.1727	39.017
	20	1	1	1	1	1	0.09968	.05140	4.5299	.1758	39.002
			1		2	1	0.09997	.05130	4.5243	.1757	39.043
BAM	01	1	1	1	1	1	0.10143	.06098	4.5151	.1776	39.063
			2			2		.06128	4.5141	.1800	39.066
	10	1	1	1	1	1		.06622	4.5205	.1805	39.030
			2			2		.06492	4.5193	.1784	39.019
	20	1	1	1	1	1		.05467	4.5179	.1761	39.030
			2			2		.05588	4.5194	.1771	39.019

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Table 2: Results of Elemental Assay
Concentrations valid for 1988-06-01

LAB	SAMPLE	STANDARD	ALIQ	FIL	^{236}U in/ug/g	^{242}Pu in/ug/g
SAL	01	NBS 960/949 (1)	1	1	503.87	4.5329
				2	504.08	4.5324
		NBS 960/949 (2)	1	1	505.34	4.5304
				2	505.27	4.5298
	10	NBS 960/949 (1)	1	1	504.84	4.5392
				2	504.53	4.5388
			2	1	504.39	4.5395
				2	504.72	4.5400
	20	NBS 960/949 (1)	1	1	505.15	4.5411
				2	505.21	4.5442
		NBS 960/949 (2)	2	1	504.04	4.5188
				2	503.93	4.5190
LEN	01	NBS 960 (1)	1	1	504.32	
				2	504.43	
		NBS 949 (1)	1	1		4.5369
				2		4.5399
	10	NBS 960 (2)	1	1	504.37	
				2	504.80	
		NBS 949 (2)	1	1		4.5379
				2		4.5370
	20	NBS 960 (3)	1	1	504.65	
				2	504.42	
		NBS 949 (3)	1	1		4.5338
				2		4.5324
SAC	01	MU1/MP1 (1)	1	1	503.74	4.5264
				2	503.71	4.5281
	10	MU1/MP1 (1)	1	1	503.89	4.5302
				2	503.94	4.5279
BAM	01	NBS 960 (1)	1	1	504.70	
				2	504.55	
		MP1/EC201 (1)	1	1		4.5442
				2		4.5442
	10	NBS 960 (1)	1	1	504.59	
				2	504.65	
		MP1/EC201 (1)	1	1		4.5449
				2		4.5446
	20	NBS 960 (1)	1	1	504.79	
				2	504.72	
		MP1/EC201 (1)	1	1		4.5376
				2		4.5387

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4. Evaluation of the Characterization Measurements

All results except the results of CENS were normalized by SAL. Results of isotopic analyses were derived by pairing measurements of unspiked and spiked aliquots obtained by the same laboratory. The normalized results of isotopic analyses are given in Table 1. The best estimate of the isotopic composition was derived from weighted laboratory means (Annex 6). SAL used this best estimate to normalize all isotope ratio measurements obtained on aliquands spiked with chemical standard solutions, except the results of CENS which were normalized by CENS against the mean of their own isotopic analyses. The normalized results of isotope dilution assays are given in Table 2.

An analysis of variance was done on the results assuming that there were subject to three independent sources of errors and that these errors were additive (Annex 6):

$$x_{ijk} = u + A_i + B_{j(i)} + C_{k(ij)} \qquad (1)$$

x_{ijk} is the result of the kth measurement on the jth sample at lab i
u is the true value of the measurement
A_i is the systematic error of laboratory i
$B_{j(i)}$ is the error for sample j
$C_{k(ij)}$ is the error for measurement and treatment k on sample j at lab i

We assume that A_i, $B_{j(i)}$ and $C_{k(ij)}$ have zero means and that their distribution may be characterized by their coefficient of variation, SA, SB and SC respectively (Table 3) (see Annex 6)

The repeatability of the measurements, SC is of the order of 0.03% for the major isotope ratios $^{233}/236$, $^{244}/242$ and for the chemical concentrations of the ^{236}U and ^{242}Pu isotopes. The sample error, SB, is of the same magnitude for $^{244}/242$; it goes up to 0.08% and 0.14% for the U and Pu assays respectively; no sample error was detected for $^{233}/236$. The coefficients of variation of the laboratory systematic errors, SA, is about 0.04% for $^{233}/236$, 0.05% for the ^{236}U concentration and 0.08% for ^{242}Pu concentration; no laboratory effect can be detected for the $^{244}/242$ ratio.

These estimates were combined as follows to calculate the relative standard error, S_i, of the mean of each laboratory, i:

$$S_i^2 = SA^2 + SB^2 \left(\sum_j N_{ij}^2 / N_i^2\right) + SC^2 / N_i \qquad (1)$$

where N_i is the total number of measurements done by laboratory i., and N_{ij} the number of measurements done by the same laboratory on sample j.

Weighted averages, X, of the laboratory means, X_i, were selected as best estimates for the composition of the QS 87 spike

$$X = \left(\sum_i W_i X_i\right) / \left(\sum_i W_i\right) \qquad (2)$$

where $W_i = 1/S_i^2$

These averages and their relative standard errors, $S = 1/\left(\sum_i W_i\right)^{1/2}$ are given in Table 4.

The calibration errors SCAL listed in the Table 4 are estimates calculated on the assumption that all results were normalized against the same reference material. For the uranium isotope ratios, the calibration errors are derived from the coefficient of variation expressing the uncertainty in the certified $^{235}/238$ ratio of NBS-U-500. For plutonium isotopes, the basis is the uncertainty in the $^{240}/239$ ratio of NBS-Pu-947. For the determination of U (or Pu) chemical concentration, the total uncertainty in the $^{233}/236$ (or $^{244}/242$) ratio assigned to QS 87 was combined with the uncertainty on the element content in the chemical reference material NBS960 or (NBS949) used for the isotope dilution analyses. Errors in the preparation of standard solutions are included in the estimate of the between laboratory effects, SA.

The total error, ST, is a simple combination of the standard error of the weighted average, S, with the calibration error, SCAL:

$$ST^2 = S^2 + SCAL^2 \qquad (3)$$

The Satterthwaites' approximation (4) was used to calculate the degrees of freedom of S_i, S and ST, assuming 20 degrees of freedom for the common calibration errors, SCAL. The calculated values, rounded to the next lower integers, were used to select the Student factor and to calculate the 95% confidence limits, also given in Table 4.

The statistical model used in this evaluation was derived by J. Jaech and is described in Annex 6.

A certificate of analysis is given in Annex 4.

Table 3: Coefficients of Variation of the Error Components (in%)

MEAS.	MEASUR. + TREAT. ERROR SC	SAMPLE . ERROR SB	LAB. EROR SA
233/236	0.028 (11)	(a)	0.035 (4)
234/236	0.10 (11)	(a)	0.094 (4)
235/236	1.2 (11)	(a)	2.7 (4)
238/236	9.8	(a)	3.7 (4)
238/242	0.20 (6)	0.88 (3)	1.2 (3)
239/242	1.1 (8)	6.4 (4)	10.7 (3)
240/242	0.049 (9)	0.091 (5)	(a)
241/242	1.1 (9)	0.80 (5)	0.97 (3)
244/242	0.037 (9)	0.029 (5)	(a)
236U Concentration	0.028 (14)	0.079 (10)	0.048 (3)
242Pu Concentration	0.024 (14)	0.14 (10)	0.084 (3)

(a) Negative variance estimate
( ) Number of degrees of freedom in parenthesis

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Table 4: Best Estimates and Confidence Limits
of the Composition of the QS 87 Spike

(Date of validity: 1989-06-01)

Measurement	Mean	S std. err. cv [%] df	SCAL cal.err. cv [%] df	ST tot. err. cv [%] df	c.l.95% c.l._rel df
U-236 [mcg/c]*	504.42	0.171205 0.034 5.7	0.17 0.034 20.0	0.24 0.048 17.5	0.51 0.10
Pu-242 [mcg/g]*	4.536	.0026829 0.059 4.1	0.0068 0.15 20.0	.0073 0.16 23.9	.015 0.33
233/236	1.0174	1.7E-04 0.017 5.4	5.1E-04 0.050 20.0	5.4E-04 0.053 23.7	0.0011 0.11
234/236	.027775	1.3E-05 0.047 6.6	9.0E-06 0.032 20.0	1.6E-05 0.057 13.3	3.4E-05 0.12
235/236	.000963	1.2E-05 1.22 4.4	1.6E-07 0.017 20.0	1.2E-05 1.22 4.4	3.3E-05 3.4
238/236	.000792	2.3E-05 2.90 13.7	2.6E-07 0.033 20.0	2.3E-05 2.90 13.7	5.0E-05 6.3
238/242	.001014	6.4E-06 0.63 5.3	2.0E-06 0.20 20.0	6.7E-06 0.66 6.3	1.6E-05 1.61
239/242	.000562	3.3E-05 5.9 4.2	1.0E-06 0.18 20.0	3.3E-05 5.89 4.2	9.2E-05 16.
240/242	.045198	1.5E-05 0.033 6.5	4.5E-05 0.10 20.0	4.7E-05 0.10 23.7	9.8E-05 0.22
241/242	.001754	1.1E-05 0.62 7.0	1.0E-06 0.057 20.0	1.1E-05 0.62 7.1	2.6E-05 1.47
244/242	0.39033	5.1E-05 0.013 11.9	3.9E-04 0.10 20.0	3.9E-04 0.10 20.7	8.2E-04 0.21

* the unit [mcg/g] means: microgram of isotope per gram of spike solution (with solution weight not corrected for air buoyancy, i.e. apparent weight as measured in air).

5. Analyses of Spent Fuel Solutions

The performance attainable in routine isotope dilution analyses using the QS 87 spike may be illustrated by the results obtained on a set of 30 spent fuel solutions received in the course of an inspection campaign (Annex 5)

Each solution was analyzed by taking duplicate samples, spiking them with QS 87, performing a redox cycle with ferrous sulfate and sodium nitrite, separating the plutonium and uranium by solvent extraction chromatography with TOPO (5), and measuring the isotope ratios on a MAT-261 spectrometer equipped with 9 collectors.

The repeatability of the mass spectrometric measurements had a mean coefficient of variation of 0.025% for uranium; and of 0.039% for plutonium; the coefficient of variation of the spiking and treatment errors was 0.048%.

6. Conclusion

The major isotope ratios of the QS 87 have been certified with relative standard deviations of 0.017% (233/236) and 0.013% (244/242), by normalization against internal standards.

A measurable between laboratory effect was observed in the measurements of the 233/236 ratio, probably due to the difficulty to measure the relative cup sensitivities of multidetector spectrometers with an accuracy of 0.01 - 0.02% (6). To improve further the precision of the certification it would be necessary also to lower the fluctuations of the blanks at masses 233, 235, 236, 238, 239, 240, 242 and 244. Normalization of the 244/242 ratio against a 238/240 or a 239/241 internal standard would be advantageous too.

To decrease the relative standard error of the ^{233}U assay (now 0.028%) and of the ^{242}Pu assay (now 0.024%) one should reduce the subsampling and treatment errors (about 0.10% now); small errors in the preparation of the chemical standard solutions are probably responsible for between laboratory effects of 0.048% and 0.084% observed in the results of uranium and plutonium assays, respectively.

However the major sources of uncertainty in the certified values are the uncertainty in the 235/238 ratio of NBS-U500 and 240/239 ratio of NBS-Pu-947. In future certifications, it would be desirable to use reference materials certified with a coefficient of variation of about 0.01% as internal standards.

Four-isotope tracers such as the QS-87 spike are also excellent internal standards for the normalization of the 235/238 and 240/239 ratio measurements when performing isotopic dilution assays with $^{235}U/^{239}Pu$ mixed spikes.

Acknowledgments

The preparation of the QS 87 spike and the contribution of the Khlopin Radium Institute were funded under TASK SSR-3-2 of the Soviet Support Programme to IAEA Safeguards.

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ANNEX 1

Results of the isotopic analysis
of U and Pu in QS 87

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R1
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SAS 11:52 TUESDAY, APRIL 4, 1989 1

certification QS87 - isotopic composition

original dataset used for the evaluations in [labsal.sas.qs87]qs87iso.ascii

OBS	EL	CLASSID	AMPOULE	SAMID	MIXID	SAMDAT	MIXDAT	ICF	R1	R2	R3	R4	R5
1	U	SAL/NBS500	A1	9142-04-103	9142-04-111	880218	880218	-0.07925	1.01687	0.0277500	0.0009747	0.00078265	.
2	U	SAL/NBS500	A1	9142-04-104	9142-04-112	880218	880218	-0.10130	1.01682	0.0277478	0.0009722	0.00079983	.
3	U	SAL/NBS500	A20	9142-06-103	9142-06-111	880219	880222	-0.01106	1.01689	0.0277553	0.0009681	0.00078662	.
4	U	SAL/NBS500	A20	9142-06-104	9142-06-112	880219	880222	-0.11854	1.01648	0.0277608	0.0009615	0.00079825	.
5	U	BAM/NBS500	A401	9628-01-101	9628-01-121	880114	880112	-0.02394	1.01699	0.0277317	0.0009138	0.00086341	.
6	U	BAM/NBS500	A401	9628-01-102	9628-01-122	880208	880208	0.04718	1.01767	0.0277622	0.0009555	0.00062441	.
7	U	BAM/NBS500	A410	9628-02-101	9628-02-121	880115	880121	0.01960	1.01786	0.0277529	0.0009262	0.00084867	.
8	U	BAM/NBS500	A410	9628-02-102	9628-02-122	880209	880209	0.04356	1.01746	0.0277542	0.0009314	0.00070938	.
9	U	BAM/NBS500	A420	9628-03-101	9628-03-121	880112	880112	0.02139	1.01741	0.0277349	0.0009152	0.00085863	.
10	U	BAM/NBS500	A420	9628-03-102	9628-03-122	880209	880209	0.02801	1.01762	0.0277566	0.0009283	0.00069161	.
11	U	SAC/NBS500/NOSAL	A320	9630-03-101	9630-03-111	880215	880215	-0.01960	1.01727	0.0278090	0.0010010	0.00087300	.
12	U	SAC/NBS500/NOSAL	A320	9630-03-101	9630-03-121	880215	880215	-0.02169	1.01767	0.0278160	0.0010010	0.00087300	.
13	U	SAC/NBS500/NOSAL	A320	9630-03-101	9630-03-131	880215	880215	-0.02379	1.01722	0.0277340	0.0009810	0.00078300	.
14	U	SAC/NBS500/NOSAL	A320	9630-03-101	9630-03-141	880215	880215	-0.00478	1.01799	0.0277480	0.0009810	0.00078300	.
15	U	LEN/NBS500	A101	9629-01-101	9629-01-111	880115	880115	-0.00010	1.01769	0.0277980	0.0009690	.	.
16	U	LEN/NBS500	A101	9629-01-102	9629-01-112	880115	880115	-0.12650	1.01765	0.0277855	0.0009668	.	.
17	U	LEN/NBS500	A110	9629-02-201	9629-02-211	880115	880115	-0.07997	1.01751	0.0278095	0.0009682	0.00079928	.
18	U	LEN/NBS500	A110	9629-02-202	9629-02-212	880115	880115	-0.06696	1.01759	0.0277408	0.0009624	0.00079306	.
19	U	LEN/RCO	QS87	9629-06-101	9629-06-211	880115	880115	0.01091	1.01756	0.0278191	0.0009601	0.00078183	.
20	U	LEN/RCO	QS87	9629-06-101	9629-06-311	880115	880115	0.02145	1.01789	0.0278249	0.0009602	0.00078166	.
21	Pu	SAL/NBS947	A1	9142-04-101	9142-04-121	880218	880218	0.03139	0.00101	0.0004922	0.0451984	0.00178776	0.390375
22	Pu	SAL/NBS947	A1	9142-04-102	9142-04-122	880218	880218	0.06657	0.00101	0.0004979	0.0452078	0.00178302	0.390391
23	Pu	SAL/NBS947	A20	9142-06-101	9142-06-121	880219	880222	0.12335	0.00103	0.0005091	0.0451767	0.00171615	0.390394
24	Pu	SAL/NBS947	A20	9142-06-102	9142-06-122	880219	880222	0.04527	0.00103	0.0004932	0.0451948	0.00176928	0.390567
25	Pu	BAM/NBS947	A401	9628-01-103	9628-01-131	880128	880129	-0.00851	0.00102	0.0006098	0.0451523	0.00180585	0.390630
26	Pu	BAM/NBS947	A401	9628-01-104	9628-01-132	880205	880205	0.04231	.	0.0006128	0.0451422	0.00182777	0.390662
27	Pu	BAM/NBS947	A410	9628-02-103	9628-02-131	880127	880127	0.06064	.	0.0006622	0.0452068	0.00183511	0.390305
28	Pu	BAM/NBS947	A410	9628-02-104	9628-02-132	880202	880206	0.06102	.	0.0006492	0.0451941	0.00181211	0.390193
29	Pu	BAM/NBS947	A420	9628-03-103	9628-03-131	880201	880129	0.04222	.	0.0005467	0.0451801	0.00178976	0.390299
30	Pu	BAM/NBS947	A420	9628-03-104	9628-03-132	880201	880129	0.04762	.	0.0005588	0.0451960	0.00179986	0.390194
31	Pu	LEN/NBS947	A101	9629-01-103	9629-01-113	871015	871015	-0.05830	0.00103	.	0.0452851	0.00181894	0.390345
32	Pu	LEN/NBS947	A101	9629-01-104	9629-01-114	871015	871015	-0.02278	0.00103	.	0.0452234	0.00176560	0.390148
33	Pu	LEN/NBS947	A110	9629-02-203	9629-02-213	871015	871015	-0.08165	0.00103	0.0006384	0.0451751	0.00180852	0.390256
34	Pu	LEN/NBS947	A110	9629-02-204	9629-02-214	871015	871015	-0.00012	0.00103	0.0006400	0.0451739	0.00181500	0.390061
35	Pu	SAC/NBS947/NOSAL	A301	9630-01-102	9630-01-211	860101	860101	-0.05375	0.00102	0.0005120	0.0451670	0.00194000	0.390441
36	Pu	SAC/NBS947/NOSAL	A301	9630-01-102	9630-01-221	860101	860101	-0.02816	0.00102	0.0005130	0.0451990	0.00194100	0.390165
37	Pu	SAC/NBS947/NOSAL	A320	9630-03-102	9630-03-211	860101	860101	-0.06967	0.00102	0.0005140	0.0453100	0.00197600	0.390016
38	Pu	SAC/NBS947/NOSAL	A320	9630-03-102	9630-03-221	860101	860101	-0.14523	0.00102	0.0005130	0.0452540	0.00197400	0.390423

P2

2

certification Q987 - isotopic composition - PLUTONIUM

isotopic decay corrected to common REFDAT = 01-JUN-88 - all ratios multiplied *1000.

OBS	CLASSID	AMPOULE	SAMID	MIXID	SAMDAT	MIXDAT	ICF	REFDAT	R82	R92	R02	R12	R42
1	BAM/NBS947	A401	9628-01-103	9628-01-131	880128	880129	-0.00851	880601	1.01426	0.609834	45.1507	1.77636	390.630
2	BAM/NBS947	A401	9628-01-104	9628-01-132	880205	880205	0.04231	880601	.	0.612775	45.1407	1.79971	390.663
3	BAM/NBS947	A410	9628-02-103	9628-02-131	880127	880127	0.06064	880601	.	0.662194	45.2052	1.80479	390.305
4	BAM/NBS947	A410	9628-02-104	9628-02-132	880202	880206	0.06102	880601	.	0.649184	45.1926	1.78405	390.194
5	BAM/NBS947	A420	9628-03-103	9628-03-131	880201	880129	0.04222	880601	.	0.546685	45.1786	1.76100	390.300
6	BAM/NBS947	A420	9628-03-104	9628-03-132	880201	880129	0.04762	880601	.	0.558795	45.1944	1.77094	390.194
7	LEN/NBS947	A101	9629-01-103	9629-01-113	871015	871015	-0.05830	880601	1.02448	.	45.2822	1.76445	390.345
8	LEN/NBS947	A101	9629-01-104	9629-01-114	871015	871015	-0.02278	880601	1.02594	.	45.2204	1.71271	390.148
9	LEN/NBS947	A110	9629-02-203	9629-02-213	871015	871015	-0.08165	880601	1.02352	0.638419	45.1722	1.75434	390.257
10	LEN/NBS947	A110	9629-02-204	9629-02-214	871015	871015	-0.00012	880601	1.02687	0.639989	45.1709	1.76063	390.061
11	SAC/NBS947/NOSAL	A301	9630-01-102	9630-01-211	860101	860101	-0.05375	880601	0.99974	0.511967	45.1557	1.72642	390.443
12	SAC/NBS947/NOSAL	A301	9630-01-102	9630-01-221	860101	860101	-0.02816	880601	0.99778	0.512967	45.1877	1.72731	390.167
13	SAC/NBS947/NOSAL	A320	9630-03-102	9630-03-211	860101	860101	-0.06967	880601	0.99680	0.513967	45.2986	1.75846	390.018
14	SAC/NBS947/NOSAL	A320	9630-03-102	9630-03-221	860101	860101	-0.14523	880601	0.99974	0.512967	45.2427	1.75668	390.425
15	SAL/NBS947	A1	9142-04-101	9142-04-121	880218	880218	0.03139	880601	1.00957	0.492196	45.1971	1.76334	390.375
16	SAL/NBS947	A1	9142-04-102	9142-04-122	880218	880218	0.06657	880601	1.01052	0.497916	45.2065	1.75867	390.392
17	SAL/NBS947	A20	9142-06-101	9142-06-121	880219	880222	0.12335	880601	1.03271	0.509086	45.1754	1.69327	390.395
18	SAL/NBS947	A20	9142-06-102	9142-06-122	880219	880222	0.04527	880601	1.03142	0.493166	45.1935	1.74569	390.567

certification QS87 - isotopic composition - PLUTONIUM

isotopic decay corrected to common REFDAT = 01-JUN-88 - all ratios multiplied *1000.

VARIANCE COMPONENT ESTIMATION PROCEDURE

CLASS LEVEL INFORMATION

.06
.70
.70
.70

CLASS	LEVELS	VALUES
CLASSID	4	BAM/NBS947 LEN/NBS947 SAC/NBS947/NOSAL SAL/NBS947
AMPOULE	7	A1 A101 A110 A20 A301 A320 A401

NUMBER OF OBSERVATIONS IN DATA SET = 18

NOTE: ALL DEPENDENT VARIABLES ARE CONSISTENT WITH RESPECT TO THE PRESENCE OR ABSENCE OF MISSING VALUES. HOWEVER, ONLY 13 OBSERVATIONS IN DATA SET CAN BE USED IN THIS ANALYSIS.

certification QS87 - isotopic composition - PLUTONIUM

isotopic decay corrected to common REFDAT = 01-JUN-88 - all ratios multiplied *1000.

VARIANCE COMPONENT ESTIMATION PROCEDURE

????NDENT VARIABLE: RS2 ??

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2

SOURCE	DF	TYPE I SS	TYPE I MS	EXPECTED MEAN SQUARE
CLASSID	3	0.00165057	0.00055019	VAR(ERROR) + 1.69230769 VAR(AMPOULE) + 3.07692308 VAR(CLASSID)
AMPOULE	3	0.00048518	0.00016173	VAR(ERROR) + 2 VAR(AMPOULE)
ERROR	6	0.00001420	0.00000237	VAR(ERROR)
CORRECTED TOTAL	12	0.00214996		

VARIANCE COMPONENT	ESTIMATE
VAR(CLASSID)	0.00013422
VAR(AMPOULE)	0.00007968
VAR(ERROR)	0.00000237

certification QS87 - isotopic composition - PLUTONIUM

isotopic decay corrected to common REFDAT = 01-JUN-88 - all ratios multiplied *1000.

VARIANCE COMPONENT ESTIMATION PROCEDURE

WT

337.76
028.32
028.32
028.32

CLASS LEVEL INFORMATION

CLASS	LEVELS	VALUES
CLASSID	4	BAM/NBS947 LEN/NBS947 SAC/NBS947/NOSAL SAL/NBS947
AMPOULE	8	A1 A110 A20 A301 A320 A401 A410 A420

NUMBER OF OBSERVATIONS IN DATA SET = 18

NOTE: ALL DEPENDENT VARIABLES ARE CONSISTENT WITH RESPECT TO THE PRESENCE OR ABSENCE OF MISSING VALUES. HOWEVER, ONLY 16 OBSERVATIONS IN DATA SET CAN BE USED IN THIS ANALYSIS.

certification QS87 - isotopic composition - PLUTONIUM

isotopic decay corrected to common REFDAT = 01-JUN-88 - all ratios multiplied *1000.

VARIANCE COMPONENT ESTIMATION PROCEDURE

????NDENT VARIABLE: R92 ??

SOURCE	DF	TYPE I SS	TYPE I MS	EXPECTED MEAN SQUARE
CLASSID	3	0.04974264	0.01658088	VAR(ERROR) + 2 VAR(AMPOULE) + 3.83333333 VAR(CLASSID)
AMPOULE	4	0.01070339	0.00267585	VAR(ERROR) + 2 VAR(AMPOULE)
ERROR	8	0.00030758	0.00003845	VAR(ERROR)
CORRECTED TOTAL	15	0.06075361		

VARIANCE COMPONENT	ESTIMATE
VAR(CLASSID)	0.00362740
VAR(AMPOULE)	0.00131870
VAR(ERROR)	0.00003845

certification QS87 - isotopic composition - PLUTONIUM

isotopic decay corrected to common REFDAT = 01-JUN-88 - all ratios multiplied *1000.

VARIANCE COMPONENT ESTIMATION PROCEDURE

CLASS LEVEL INFORMATION

CLASS	LEVELS	VALUES
CLASSID	4	BAM/NBS947 LEN/NBS947 SAC/NBS947/NOSAL SAL/NBS947
AMPOULE	9	A1 A101 A110 A20 A301 A320 A401 A410 A420

NUMBER OF OBSERVATIONS IN DATA SET = 18

certification QS87 - isotopic composition - PLUTONIUM

isotopic decay corrected to common REFDAT = 01-JUN-88 - all ratios multiplied *1000.

VARIANCE COMPONENT ESTIMATION PROCEDURE

????NDENT VARIABLE: R02 ??

SOURCE	DF	TYPE I SS	TYPE I MS	EXPECTED MEAN SQUARE
CLASSID	3	0.00560308	0.00186769	VAR(ERROR) + 2 VAR(AMPOULE) + 4.44444444 VAR(CLASSID)
AMPOULE	5	0.01955604	0.00391121	VAR(ERROR) + 2 VAR(AMPOULE)
ERROR	9	0.00444856	0.00049428	VAR(ERROR)
CORRECTED TOTAL	17	0.02960768		

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86695

VARIANCE COMPONENT	ESTIMATE
VAR(CLASSID)	-0.00045979
VAR(AMPOULE)	0.00170846
VAR(ERROR)	0.00049428

certification QS87 - isotopic composition - PLUTONIUM

isotopic decay corrected to common REFDAT = 01-JUN-88 - all ratios multiplied *1000.

VARIANCE COMPONENT ESTIMATION PROCEDURE

CLASS LEVEL INFORMATION

CLASS	LEVELS	VALUES
CLASSID	4	BAM/NBS947 LEN/NBS947 SAC/NBS947/NOSAL SAL/NBS947
AMPOULE	9	A1 A101 A110 A20 A301 A320 A401 A410 A420

NUMBER OF OBSERVATIONS IN DATA SET = 18

certification QS87 - isotopic composition - PLUTONIUM

isotopic decay corrected to common REFDAT = 01-JUN-88 - all ratios multiplied *1000.

VARIANCE COMPONENT ESTIMATION PROCEDURE

????NDENT VARIABLE: R12 ??

SOURCE	DF	TYPE I SS	TYPE I MS	EXPECTED MEAN SQUARE
CLASSID	3	0.00631252	0.00210417	VAR(ERROR) + 2 VAR(AMPOULE) + 4.44444444 VAR(CLASSID)
AMPOULE	5	0.00391564	0.00078313	VAR(ERROR) + 2 VAR(AMPOULE)
ERROR	9	0.00328214	0.00036468	VAR(ERROR)
CORRECTED TOTAL	17	0.01351031		

VARIANCE COMPONENT	ESTIMATE
VAR(CLASSID)	0.00029724
VAR(AMPOULE)	0.00020922
VAR(ERROR)	0.00036468

certification Q987 - isotopic composition - PLUTONIUM

isotopic decay corrected to common REFDAT = 01-JUN-88 - all ratios multiplied *1000.

VARIANCE COMPONENT ESTIMATION PROCEDURE

CLASS LEVEL INFORMATION

CLASS	LEVELS	VALUES
CLASSID	4	BAM/NBS947 LEN/NBS947 SAC/NBS947/NOSAL SAL/NBS947
AMPOULE	9	A1 A101 A110 A20 A301 A320 A401 A410 A420

NUMBER OF OBSERVATIONS IN DATA SET = 18

certification QS87 - isotopic composition - PLUTONIUM

isotopic decay corrected to common REFDAT = 01-JUN-88 - all ratios multiplied *1000.

lab means with variance and weight - 238:242

OBS	CLASSID	XQQ	NI	SUMNIJSQ	SASQ	SBSQ	SCSQ	INVNI	FSB	VAR	WT
1	BAM/NBS947	1.01426	1	1	0.00013422	0.00007968	0.00000237	1.00	1.0	0.000216270	4623.85
2	LEN/NBS947	1.02520	4	8	0.00013422	0.00007968	0.00000237	0.25	0.5	0.000174653	5725.66
3	SAC/NBS947/NOSAL	0.99851	4	8	0.00013422	0.00007968	0.00000237	0.25	0.5	0.000174653	5725.66
4	SAL/NBS947	1.02106	4	8	0.00013422	0.00007968	0.00000237	0.25	0.5	0.000174653	5725.66

????????? certification QS87 - isotopic composition - PLUTONIUM

isotopic decay corrected to common REFDAT = 01-JUN-88 - all ratios multiplied *1000.

VARIANCE COMPONENT ESTIMATION PROCEDURE

????NDENT VARIABLE: R42 ??

SOURCE	DF	TYPE I SS	TYPE I MS	EXPECTED MEAN SQUARE
CLASSID	3	0.13958519	0.04652840	VAR(ERROR) + 2 VAR(AMPOULE) + 4.44444444 VAR(CLASSID)
AMPOULE	5	0.23536061	0.04707212	VAR(ERROR) + 2 VAR(AMPOULE)
ERROR	9	0.18671798	0.02074644	VAR(ERROR)
CORRECTED TOTAL	17	0.56166377		

VARIANCE COMPONENT	ESTIMATE
VAR(CLASSID)	-0.00012234
VAR(AMPOULE)	0.01316284
VAR(ERROR)	0.02074644

certification QS87 - isotopic composition - PLUTONIUM

isotopic decay corrected to common REFDAT = 01-JUN-88 - all ratios multiplied *1000.

grand mean with variance and degrees of freedom for grand mean variance - 238:242

dftot is calculated by SATTERTHWAITE's approximation according to JAECH's suggestion

OBS	R	XQQQ	SUMWT	SUMFSB	SUMINVNI	VARXQQQ	SASQ	SBSQ	SCSQ	P1	R1
1	4	1.01478	21800.8	2.5	1.75	0.0000456698	0.00013422	0.00007968	0.00000237	1.69231	3.07692

OBS	P2	MA	MB	MC	FA	FB	FC	NUEC	NUEB	NUEA	GA	GB	GC	DFTOT
1	2	0.00055019	0.00016173	0.00000237	3	3	6	6	2.91241	1.5918	0.25	0.15625	0.109375	2.7664

certification QS87 - isotopic composition - PLUTONIUM

isotopic decay corrected to common REFDAT = 01-JUN-88 - all ratios multiplied *1000.

lab means with variance and weight - 239:242

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OBS	CLASSID	XQQ	NI	SUMNIJSQ	SASQ	SBSQ	SCSQ	INVNI	F3B	VAR	WT
1	BAM/NBS947	0.606578	6	12	0.0036274	0.0013187	0.00003845	0.166667	0.33333	0.00407338	245.497
2	LEN/NBS947	0.639204	2	4	0.0036274	0.0013187	0.00003845	0.500000	1.00000	0.00496533	201.397
3	SAC/NBS947/NOSAL	0.512967	4	8	0.0036274	0.0013187	0.00003845	0.250000	0.50000	0.00429636	232.755
4	SAL/NBS947	0.498091	4	8	0.0036274	0.0013187	0.00003845	0.250000	0.50000	0.00429636	232.755

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certification QS87 - isotopic composition - PLUTONIUM

isotopic decay corrected to common REFDAT = 01-JUN-88 - all ratios multiplied *1000.

grand mean with variance and degrees of freedom for grand mean variance - 239:242

dftot is calculated by SATTERTHWAITE's approximation according to JAECH's suggestion

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7143 2

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665

OBS	R	XQQQ	SUMWT	SUMFSB	SUMINVNI	VARXQQQ	SASQ	SBSQ	SCSQ	P1	R1	P2
1	4	0.562224	912.403	2.33333	1.16667	0.00109601	0.0036274	0.0013187	0.00003845	2	3.83333	2

OBS	MA	MB	MC	FA	FB	FC	NUEC	NUEB	NUEA	GA	GB	GC	DFTOT
1	0.0165809	0.00267585	0.00003845	3	4	8	8	3.88547	2.06941	0.25	0.145833	0.0729167	2.95204

certification QS87 - isotopic composition - PLUTONIUM

isotopic decay corrected to common REFDAT = 01-JUN-88 - all ratios multiplied *1000.

P2

3 2

lab means with variance and weight - 240:242

OBS	CLASSID	XQQ	NI	SUMNIJSQ	SASQ	SBSQ	SCSQ	INVNI	FSB	VAR	WT
1	BAM/NBS947	45.1770	6	12	0	0.00170846	0.00049428	0.166667	0.333333	0.000651867	1534.06
2	LEN/NBS947	45.2114	4	8	0	0.00170846	0.00049428	0.250000	0.500000	0.000977800	1022.70
3	SAC/NBS947/NOSAL	45.2212	4	8	0	0.00170846	0.00049428	0.250000	0.500000	0.000977800	1022.70
4	SAL/NBS947	45.1931	4	8	0	0.00170846	0.00049428	0.250000	0.500000	0.000977800	1022.70

certification QS87 - isotopic composition - PLUTONIUM

isotopic decay corrected to common REFDAT = 01-JUN-88 - all ratios multiplied *1000.

grand mean with variance and degrees of freedom for grand mean variance - 240:242

dftot is calculated by SATTERTHWAITE's approximation according to JAECH's suggestion

OBS	R	XQQQ	SUMWT	SUMFSB	SUMINVNI	VARXQQQ	SASQ	SBSQ	SCSQ	P1	R1	P2
1	4	45.1981	4602.17	1.83333	0.916667	0.000217289	0	0.00170846	0.00049428	2	4.44444	2

OBS	MA	MB	MC	FA	FB	FC	NUEC	NUEB	NUEA	GA	GB	GC	DFTOT
1	0.00186769	0.00391121	0.00049428	3	5	9	9	3.78252	1	0.25	0.114583	0.0572917	4.61956

certification QS87 - isotopic composition - PLUTONIUM

isotopic decay corrected to common REFDAT = 01-JUN-88 - all ratios multiplied *1000.

lab means with variance and weight - 241:242

OBS	CLASSID	XQQ	NI	SUMNIJSQ	SASQ	SBSQ	SCSQ	INVNI	FSB	VAR	WT
1	BAN/NBS947	1.78281	6	12	0.00029724	0.00020922	0.00036468	0.166667	0.333333	0.00042776	2337.76
2	LEN/NBS947	1.74803	4	8	0.00029724	0.00020922	0.00036468	0.250000	0.500000	0.00049302	2028.32
3	SAC/NBS947/NOSAL	1.74222	4	8	0.00029724	0.00020922	0.00036468	0.250000	0.500000	0.00049302	2028.32
4	SAL/NBS947	1.74024	4	8	0.00029724	0.00020922	0.00036468	0.250000	0.500000	0.00049302	2028.32

QS87

certification QS87 - isotopic composition - PLUTONIUM

isotopic decay corrected to common REFDAT = 01-JUN-88 - all ratios multiplied *1000.

grand mean with variance and degrees of freedom for grand mean variance - 241:242

dftot is calculated by SATTERTHWAITE's approximation according to JAECH's suggestion

OBS	R	XQQQ	SUMWT	SUMFSB	SUMINVNI	VARXQQQ	SASQ	SBSQ	SCSQ	P1	R1	P2
1	4	1.75441	8422.71	1.83333	0.916667	0.000118727	0.00029724	0.00020922	0.00036468	2	4.44444	2

OBS	MA	MB	MC	FA	FB	FC	NUEC	NUEB	NUEA	GA	GB	GC	DFTOT
1	0.00210417	0.00078313	0.00036468	3	5	9	9	1.274	1.07196	0.25	0.114583	0.0572917	2.49448

certification QS87 - isotopic composition - PLUTONIUM

isotopic decay corrected to common REFDAT = 01-JUN-88 - all ratios multiplied *1000.

lab means with variance and weight - 244:242

OBS	CLASSID	XQQ	NI	SUMNIJSQ	SASQ	SBSQ	SCSQ	INVNI	FSB	VAR	WT
1	BAM/NBS947	390.381	6	12	0	0.0131628	0.0207464	0.166667	0.333333	0.0078454	127.464
2	LEN/NBS947	390.203	4	8	0	0.0131628	0.0207464	0.250000	0.500000	0.0117680	84.976
3	SAC/NBS947/NOSAL	390.263	4	8	0	0.0131628	0.0207464	0.250000	0.500000	0.0117680	84.976
4	SAL/NBS947	390.432	4	8	0	0.0131628	0.0207464	0.250000	0.500000	0.0117680	84.976

certification QS87 - isotopic composition - PLUTONIUM

isotopic decay corrected to common REFDAT = 01-JUN-88 - all ratios multiplied *1000.

grand mean with variance and degrees of freedom for grand mean variance - 244:242

dftot is calculated by SATTERTHWAITE's approximation according to JAECH's suggestion

OBS	R	XQQQ	SUMWT	SUMFSB	SUMINVNI	VARXQQQ	SASQ	SBSQ	SCSQ	P1	R1	P2
1	4	390.326	382.392	1.83333	0.916667	0.00261512	0	0.0131628	0.0207464	2	4.44444	2

OBS	MA	MB	MC	FA	FB	FC	NUEC	NUEB	NUEA	GA	GB	GC	DFTOT
1	0.0465284	0.0470721	0.0207464	3	5	9	9	1.41154	1	0.25	0.114583	0.0572917	3.86695

ANNEX 2

Results of the Determination of U and Pu Concentrations in QS 87

Table 2

certification 0887 - element assay 12:37 MONDAY, JUNE 19, 1989 1

EL-Pu LABNAM-BAM

OBS	STD_NAME	AMPOULE	ANALDATE	ASSAY	UNIT	SAL_ID
1	EC210	A401	05FEB1988	4.54420	mgPu-242/g	9142-09-212
2	EC210	A401	29JAN1988	4.54420	mgPu-242/g	9142-09-211
3	EC210	A410	06FEB1988	4.54490	mgPu-242/g	9142-09-222
4	EC210	A410	27JAN1988	4.54460	mgPu-242/g	9142-09-221
5	EC210	A420	05FEB1988	4.53760	mgPu-242/g	9142-09-232
6	EC210	A420	30JAN1988	4.53870	mgPu-242/g	9142-09-231

EL-Pu LABNAM-RI

OBS	STD_NAME	AMPOULE	ANALDATE	ASSAY	UNIT	SAL_ID
7	NBS949(LAB)	A101	15JAN1988	4.53690	mgPu-242/g	9142-08-322
8	NBS949(LAB)	A101	15JAN1988	4.53990	mgPu-242/g	9142-08-321
9	NBS949(LAB)	A110	15JAN1988	4.53790	mgPu-242/g	9142-08-342
10	NBS949(LAB)	A110	15JAN1988	4.53700	mgPu-242/g	9142-08-341
11	NBS949(LAB)	A120	15JAN1988	4.53380	mgPu-242/g	9142-08-362
12	NBS949(LAB)	A120	15JAN1988	4.53240	mgPu-242/g	9142-08-361

EL-Pu LABNAM-SACLAY

OBS	STD_NAME	AMPOULE	ANALDATE	ASSAY	UNIT	SAL_ID
13	MP1	A301	15MAR1988	4.52640	mgPu-242/g	9142-11-431
14	MP1	A301	15MAR1988	4.52810	mgPu-242/g	9142-11-432
15	MP1	A310	15MAR1988	4.53020	mgPu-242/g	9142-11-441
16	MP1	A310	15MAR1988	4.52790	mgPu-242/g	9142-11-442

EL-Pu LABNAM-SAL

OBS	STD_NAME	AMPOULE	ANALDATE	ASSAY	UNIT	SAL_ID
17	CL87	A10_1	19FEB1988	4.53920	mgPu-242/g	9142-08-132
18	CL87	A10_1	19FEB1988	4.53880	mgPu-242/g	9142-08-131
19	CL87	A10_2	19FEB1988	4.53950	mgPu-242/g	9142-08-142
20	CL87	A10_2	19FEB1988	4.54000	mgPu-242/g	9142-08-141
21	CL87	A1_1	18FEB1988	4.53290	mgPu-242/g	9142-08-112
22	CL87	A1_1	18FEB1988	4.53240	mgPu-242/g	9142-08-111
23	CL84	A1_2	19FEB1988	4.53040	mgPu-242/g	9142-08-122
24	CL84	A1_2	18FEB1988	4.52980	mgPu-242/g	9142-08-121
25	CL87	A20_1	22FEB1988	4.54110	mgPu-242/g	9142-08-152
26	CL87	A20_1	22FEB1988	4.54420	mgPu-242/g	9142-08-151
27	CL84	A20_2	22FEB1988	4.51880	mgPu-242/g	9142-08-162
28	CL84	A20_2	22FEB1988	4.51900	mgPu-242/g	9142-08-161

Table 2 (ct'd)

EL=U LABNAM=BAH

OBS	STD_NAME	AMPOULE	ANALDATE	ASSAY	UNIT	SAL_ID
29	NBS960(LAB)	A401	12JAN1988	504.700	mgU-236/g	9142-07-212
30	NBS960(LAB)	A401	12JAN1988	504.550	mgU-236/g	9142-07-211
31	NBS960(LAB)	A410	21JAN1988	504.590	mgU-236/g	9142-07-232
32	NBS960(LAB)	A410	21JAN1988	504.650	mgU-236/g	9142-07-231
33	NBS960(LAB)	A420	12JAN1988	504.790	mgU-236/g	9142-07-252
34	NBS960(LAB)	A420	12JAN1988	504.720	mgU-236/g	9142-07-251

EL=U LABNAM=RI

OBS	STD_NAME	AMPOULE	ANALDATE	ASSAY	UNIT	SAL_ID
35	NBS960(LAB)	A101	15JAN1988	504.320	mgU-236/g	9142-07-322
36	NBS960(LAB)	A101	15JAN1988	504.430	mgU-236/g	9142-07-321
37	NBS960(LAB)	A110	15JAN1988	504.370	mgU-236/g	9142-07-342
38	NBS960(LAB)	A110	15JAN1988	504.800	mgU-236/g	9142-07-341
39	NBS960(LAB)	A120	15JAN1988	504.650	mgU-236/g	9142-07-362
40	NBS960(LAB)	A120	15JAN1988	504.420	mgU-236/g	9142-07-361

EL=U LABNAM=SACLAY

OBS	STD_NAME	AMPOULE	ANALDATE	ASSAY	UNIT	SAL_ID
41	MU1	A301	15MAR1988	503.740	mgU-236/g	9142-10-411
42	MU1	A301	15MAR1988	503.710	mgU-236/g	9142-10-412
43	MU1	A310	15MAR1988	503.890	mgU-236/g	9142-10-421
44	MU1	A310	15MAR1988	503.940	mgU-236/g	9142-10-422

EL=U LABNAM=SAL

OBS	STD_NAME	AMPOULE	ANALDATE	ASSAY	UNIT	SAL_ID
45	CL87	A10_1	22FEB1988	504.840	mgU-236/g	9142-07-132
46	CL87	A10_1	19FEB1988	504.530	mgU-236/g	9142-07-131
47	CL87	A10_2	19FEB1988	504.390	mgU-236/g	9142-07-142
48	CL87	A10_2	19FEB1988	504.720	mgU-236/g	9142-07-141
49	CL87	A1_1	18FEB1988	503.870	mgU-236/g	9142-07-112
50	CL87	A1_1	18FEB1988	504.080	mgU-236/g	9142-07-111
51	CL84	A1_2	19FEB1988	505.340	mgU-236/g	9142-07-122
52	CL84	A1_2	18FEB1988	505.270	mgU-236/g	9142-07-121
53	CL87	A20_1	22FEB1988	505.150	mgU-236/g	9142-07-152
54	CL87	A20_1	22FEB1988	505.210	mgU-236/g	9142-07-151
55	CL84	A20_2	22FEB1988	504.040	mgU-236/g	9142-07-162
56	CL84	A20_2	22FEB1988	503.930	mgU-236/g	9142-07-161

EL-Pu

VARIANCE COMPONENT ESTIMATION PROCEDURE

CLASS LEVEL INFORMATION

CLASS	LEVELS	VALUES
LABNAM	4	BAM RI SACLAY SAL
AMPOULE	14	A101 A10_1 A10_2 A110 A120 A1_1 A1_2 A20_1 A20_2 A301 A310 A401 A410 A420

NUMBER OF OBSERVATIONS IN BY GROUP = 28

EL-Pu

VARIANCE COMPONENT ESTIMATION PROCEDURE

????NDENT VARIABLE: ASSAY ??

SOURCE	DF	TYPE I SS	TYPE I MS	EXPECTED MEAN SQUARE
LABNAM	3	0.00053565	0.00017855	VAR(ERROR) + 2 VAR(AMPOULE) + 6.57142857 VAR(LABNAM)
AMPOULE	10	0.00084438	0.00008444	VAR(ERROR) + 2 VAR(AMPOULE)
ERROR	14	0.00001596	0.00000114	VAR(ERROR)
CORRECTED TOTAL	27	0.00139599		

VARIANCE COMPONENT	ESTIMATE
VAR(LABNAM)	0.00001432
VAR(AMPOULE)	0.00004165
VAR(ERROR)	0.00000114

EL=U

VARIANCE COMPONENT ESTIMATION PROCEDURE

CLASS LEVEL INFORMATION

CLASS	LEVELS	VALUES
LABNAM	4	BAM RI SACLAY SAL
AMPOULE	14	A101 A10_1 A10_2 A110 A120 A1_1 A1_2 A20_1 A20_2 A301 A310 A401 A410 A420

NUMBER OF OBSERVATIONS IN BY GROUP = 28

Plutonium

EL-U

VARIANCE COMPONENT ESTIMATION PROCEDURE

????NDENT VARIABLE: ASSAY ??

SOURCE	DF	TYPE I SS	TYPE I MS	EXPECTED MEAN SQUARE
LABNAM	3	2.16806310	0.72268770	VAR(ERROR) + 2 VAR(AMPOULE) + 6.57142857 VAR(LABNAM)
AMPOULE	10	3.32830833	0.33283083	VAR(ERROR) + 2 VAR(AMPOULE)
ERROR	14	0.27700000	0.01978571	VAR(ERROR)
CORRECTED TOTAL	27	5.77337143		

VARIANCE COMPONENT	ESTIMATE
VAR(LABNAM)	0.05932604
VAR(AMPOULE)	0.15652256
VAR(ERROR)	0.01978571

Uranium

Plutonium

grand mean - weighted averaging and calculation of associated standard error according to Jaech's proposal based on Satterthwaite's model

OBS	R	XQQQ	SUMWT	SUMFSR	SUMINVWI	VARXQQQ	SASQ	SBSQ	SCSQ	F1	R1	F2
1	4	4.5354	145488	1.33333	0.666667	.000006873444	0.00001432	0.00004165	0.00000114	2	6.57143	2

OBS	MA	MB	MC	FA	FB	FC	NUEC	NUEB	NUEA	QA	QB	QC	DFTOT
1	0.00017855	0.00008444	0.00000114	3	10	14	14	9.73054	0.780902	0.25	0.0833333	0.0416667	2.67665

Uranium

grand mean - weighted averaging and calculation of associated standard error
according to Jaech's proposal based on Satterthwaite's model

OBS	R	XQQQ	SUMWT	SUMFSB	SUMINVNI	VARXQQQ	SASQ	SBSQ	SCSQ	P1	R1	P2
1	4	504.444	35.9239	1.33333	0.666667	0.0278366	0.059326	0.156523	0.0197857	2	6.57143	2

OBS	MA	MB	MC	FA	FB	FC	NUEC	NUED	NUEA	GA	GB	GC	DFTOT
1	0.722688	0.332831	0.0197857	3	10	14	14	8.82413	0.820556	0.25	0.0833333	0.0416667	2.69609

ANNEX 3

Preparation of the QS 87 Spike

QS 87

Khlopin Radium Institute SCUAE USSR

M.Rychinskii, L.Buljanitss, A.Lovtsus, A.Stepanov and E.Beljaev

DEVELOPMENT OF URANIUM AND PLUTONIUM STANDARDS (QS 87) USED AS COMPLEX LABEL WHEN ANALYSING SPENT NUCLEAR FUEL

(Task SSR-3-2 of the USSR Support Programme)

Leningrad 1988

ABSTRACT

The preparation of reference material (RM), solution of uranium and plutonium (QS 87) in Radium Institute is described. The RM is the mixture of U-233, U-236, Pu-242 and Pu-244 . It is designed for use as a spike for mass spectrometric measurements with isotope dilution.The RM is transmitted to IAEA for use in savegurds purposes

June 1988

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INTRODUCTION

The objective of this work was the preparation and determination of isotopic ratios U-233/U-236, Pu-244/Pu-242 and element concentrations in the reference material - solution of uranium and plutonium. The reference material was named QS87. The reference material was designed to use as internal standard in mass spectrometric analysis of uranium and plutonium in spent fuel solutions.

The task was fulfiled in the framewdrk of the USSR support programme (Task No SSR-3-2).

The preparation of QS87 was carried out in Radium Institute (RI); the materials were characterised in RI,SAL,SEAIN (France) and BAM (W.Berlin).

The prepared RM QS87 was sent to IAEA on July 1987 to use for the safeguards purposes.

1. Stages of the work

The RM QS87 should have the following characteristics:

Isotopic concentrations -

U-233	-	0.5 mg/g
U-236	-	0.5 mg/g
Pu-242	-	0.005 mg/g
Pu-244	-	0.002 mg/g

Concentration of HNO_3 - 7 M

Volume of solution - 2 l

Number of ampoules - 20

On the first stage of the work two solutions had to be prepared. One of them should contain uranium isotopes. another one - plutonium isotopes

After the analysis of these solutions had been made by RI,SAL and SEAIN they should be mixed (in the case of good coincidence of the results) and conditioned according to the volumes and concentrations desired. Then the mixture (QS87) should be sealed in ampoules and transmitted to IAEA. The analysis of QS87 had to be done by RI,SAL and one or two network laboratories. The certification of QS87 had to be done on the basis of the results obtained by the laboratories mentioned above

2. Initial materials and preparation of double mixtures

2.1 Solution of the mixture of U-233 and U-236

The solution of SRM U-233 (FCO 3213-85) and nitrate solution of oxide-peroxide of U-236 were used as the initial materials. Both of them were prepared in USSR. The isotopic composition of these materials are shown in Table 1.

The content of the plutonium in the uranium initial materials was determined in order to take into account its presence in calcilations of the total plutonium concentration in QS87. This is important too for the determination of the interference effects in mass spectrometric measurements. The isotope dilution method.with alpha spectrometry was used in plutonium determinations.The solution of Pu-236 with the specific activity 1.88 Bq/ml was used as a spike. Results obtained from this analysis are as follows (in molar ratios):

Pu-239/U-233	-	$7*10^{-7}$
Pu-239/U-236	-	$1.4*10^{-8}$
Pu-238/U-233	-	$<3*10^{-9}$
Pu-238/U-236	-	$4*10^{-10}$

As the plutonium content was determined to be very small the decision was taken not to purify the uranium initial materials. The blending of the uranium solutions were carried out with mass control on all stages of the procedure.

2.2 Solution of Pu-242 and Pu-244 mixture

The initial materials of plutonium were the working reference material Pu-242 (nitrate solution, CO -009-87) prepared in RI and Pu-244 NBS 996 provided by IAEA. The isotopic composition is shown in Table 2.

After dissolution the standard NBS 996 was mixed with the solution of Pu-242. The isotopic exchange was carried out by means of redox cycle with N_2H_4 HNO_3. An anion exchange procedure was used for separation of americium. The process was carried out on the column with the resin VP-1 in 7 M HNO_3. The chemical yield of plutonium was 95%. The solution of plutonium double mixture was analysed for determination of uranium impurity. The laser induced luminescence at 527 nm in polysilicate solution media was used for this purpose. The solution of uranium SRM FCO 2893-84 was used for calibration. The determined content of uranium in plutonium expressed as mass ratio was $(1.9 \pm 0.3) * 10^{-5}$

3. Mass spectrometric measurements

The number of aliquots, their codes and weights are shown in Fig. 1 and 2. The indexes (1) and (2) in the names of SRM denote that the different specimens were used, e.g. NBS U-500 (1) and NBS U-500 (1) were acquired with the difference in five years.

For the samples in which NBS 947 and NBS 949 were used the isotopic exchange procedure were carried out (see item 2.2).

The mass spectrometric measurements were carried out with TH-5 mass spectrometer. For measurement of each sample two loadings were used. Each loading required about 10 mkg of uranium and 1 mkg of plutonium. 5 series of measurements were carried out per one loading. Each series consisted of 10-15 scans.In other words, each loading produced 50-70 scans.Inside the time intervals between the series the focusing of ion source and the peak positions were checked. The results of mass spectrometric measurements are shown in Tables 3 and 4.

4. Data processing

4.1. Calculation of isotopic ratios with use of internal standard

On the basis of material balance the following equation can be written for example for uranium /1/:

$$\frac{N_n^6}{N_t^6} = \frac{R_m^{3/6} - R_t^{3/6}}{R_n^{3/6} - R_m^{3/6}} = \frac{R_m^{5/6} - R_t^{5/6}}{R_n^{5/6} - R_m^{5/6}} = \frac{R_m^{8/6} - R_t^{8/6}}{R_n^{8/6} - R_m^{8/6}} \quad (1)$$

Indexes n, m and t are related to the analysed sample, mixture of the sample with standard reference material and reference material respectively, N_n^6 and N_t^6 are the quantities of moles of 236U in analysed sample and SRM; $R^{3/6}$, $R^{5/6}$ and $R^{8/6}$ - 'true' values of molar isotopic ratios of one of three isotopes - 233U,235U and 238U to the fourth - 236U.

The relation between 'true' and measured isotopic ratios can be expressed by means of following equations (for example for $R^{3/6}$):

$$R_n^{3/6} = R_n^{3/6*} * (1 + \Delta_{3/6} * F_n) \quad (2)$$

$$R_m^{3/6} = R_m^{3/6*} * (1 + \Delta_{3/6} * F_m) \quad (3)$$

Index * is related to the measured ratios, $\Delta_{3/6}$ is the difference of mass number for isotopes in denominator and in nominator (in expressions (2) and (3) $\Delta_{3/6} = 3$), F_n and F_m are discrimination factors (bias corrections) per one mass unit for the analysed sample and the mixture of the sample with SRM respectively. The aim of data processing is to determine 'true' ratios in the sample if the measured ratios for the

sample as well for the mixture of the sample with the SRM and the 'true' ratios in SRM are known.

The substitution (2) and (3) into the second part of (1) leads to expression for two first parts of (1):

$$R_m^{3/6*} *(1+ \Delta_{3/6} *F_m) - R_t^{3/6} = Q*R_n^{3/6*} * (1+ \Delta_{3/6} *F_n) -$$

$$- Q*R_m^{3/6*} *(1+ \Delta_{3/6} *F_m) \qquad (4)$$

where $Q = N_n^6 / N_t^6$

Rewrite (4) in the form:

$$\Delta_{3/6} *R_m^{3/6*} *(F_m + Q*F_m) + (R_m^{3/6*} - R_n^{3/6*})*Q -$$

$$- \Delta_{3/6} *R_n^{3/6*} *Q*F_n = R_t^{3/6} - R_m^{3/6*} \qquad (5)$$

Denoting

$$F_m *(1+Q) = X_1 \qquad (6)$$

$$Q = X_2 \qquad (7)$$

$$Q*F_n = X_3 \qquad (8)$$

and taking into account (1) one can write the system of three linear equation:

$$\Delta_{3/6} *R_m^{3/6*} *X_1 + (R_m^{3/6*} - R_n^{3/6*})*X_2 - \Delta_{3/6} *R_n^{3/6*} *X_3 =$$

$$= R_t^{3/6} - R_m^{3/6*} \qquad (9)$$

$$\Delta_{5/6} *R_m^{5/6*} *X_1 + (R_m^{5/6*} - R_n^{5/6*})*X_2 - \Delta_{5/6} *R_n^{5/6*} *X_3 =$$

$$= R_t^{5/6} - R_m^{5/6*} \qquad (10)$$

$$\Delta_{8/6} *R_m^{8/6*} *X_1 + (R_m^{8/6*} - R_n^{8/6*})*X_2 - \Delta_{8/6} *R_n^{8/6*} *X_3 =$$

$$= R_t^{8/6} - R_m^{8/6*} \qquad (11)$$

The solution of these equations in relation to X_1, X_2 and X_3 and combination with (6)-(8) give F_n, F_m and Q. Combination with (1)-(3) gives 'true' isotopic ratios for sample (R_n) for the mixture and the quantity of moles of analyzed isotope (236U for example) in the sample.

4.2 Results of calculation

The following initial data needed for the calibration were used: the certified values for SRM's (NBS U-500, NBS 947), the mean values of measured isotopic ratios in the sample - R_n^* and measured isotopic ratios in mixture - R_m^*. The values $R_n^{3/6*}$ and $R_n^{4/2*}$ are the mean values of 6 loadings: 101, 102, 131, 132, 231, 232 (Table 3, 4). Other values R_n^* are the mean values of 2 loading: 101 and 102. The calculation was carried out in correspondence with the scheme in item 4.1. Two other methods of calculation were used: the iteration procedure proposed by S.Deron and the transformation (1)-(3) into quadratic equation where F_n was the root. All three methods of calculation gave the similar results (within 7 digits). The initial data and the results of calculation i.e. corrected (normalized) isotopic ratios are given in Table 5, 6.

4.3. Calculation of element concentrations

For these calculation the equation for isotopic dilution was used. For example in the case of uranium the following equation is valid:

$$\frac{N_n^6}{N_t^8} = \frac{R_m^{6/8} - R_t^{6/8}}{1 - R_m^{6/8}/R_n^{6/8}} \qquad (12)$$

In right part of this equation only $R_m^{6/8}$ is unknown since $R_n^{6/8}$ had been found out in item 4.2. For derivation this equation the next procedure was used. First of all F_m must be found out.

Since in SRM NBS 960 there are neither 233U nor 236U, $R_n^{3/6}=R_m^{3/6}$ and the following expression can be written:

$$R_n^{3/6} = R_m^{3/6} = R_m^{3/6*} *(1+3F_m) \qquad (13)$$

For caiculation $R_m^{6/8}$ the next expression was used:

$$R_m^{6/8} = R_m^{6/8*} *(1+2F_m) \qquad (14)$$

After substitution (14) into (12) N_n^6 can be found. Using isotopic ratios (Tables 5, 6) weights of SRM added into the samole concentration of uranium in SRM and weights of the sample (Fig. 1.2) the concentration of uranium in the sample can be found.

The procedure of calculation of plutonium concentration was similar with the exception of special allowance made for the presence of 0.006% 242Pu in SRM NBS 949f when the calculation of $R_n^{4/2}$ (eq. (13)) was progress. The weights of SRM NBS 949f and aliquots of the sample were taken into account too. The calculation values of uranium and plutonium concentrations are given in Table 7.

The concentration of uranium was determined also by means of potentiometric titration with use Davies-Gray-NBL technique. 3 mg of uranium was needed for one determination. Simultaneously the titration of the solution of NBS 960 was carried out. The titratior Mettler DL40RC was in use. The mean value of uranium concentration obtained by this method was 2.0078 mg/g for 5 determinations with SD 0.0017 mg/g *). It is seen that the values obtained by isotopic dilution and titration coincide within the 95% confidence limits.

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*) This part of work was carried out with Mr. H.Aigner's participation.

5. Comparison of the results obtained by RI, SAL and SEAIN

The obtained resultes are shown in Table 8. The values of major ratios (233/236 and 244/242) are in good agreement for all laboratories. On this basis it was decided to prepare QS87 by mixing the double solutions.

6. Preparation of QS87

The procedure was as follows. To 1243.05 g of solution of uranium mixture in 2.5 l flask, 420.166 g of plutonium double mixture solution and 769.384 g 16 M HNO_3 were added. All operations of transference and dilution were carried with weight control. The final solution of QS87 was weighed with the error less than +-0.3 g. The prepared solution was agitated for 5 days and then packed into 20 ampoules made of 'pyrex' glass. Each ampoule was filled with about 100 ml of solution. Just after filling ampoules were sealed. In the beginning, in the middle and in the end of filling process (which duration was about 1 hour) the solution of QS87 was aliquoted into small ampouls (approximately 4 g of solution per ampoule) which were sealed too. The scheme of packing is shown on Fig. 3. 20 big ampoules (A1-A20) and part of small ampoules were transmitted to SAL. The ampoules A101, A110 and A120 were analysed in RI. The scheme of analysis in RI are shown on Fig. 4-6.

7. Chemical treatment of the samples

Anion exchange resin Dowex 2*8(100-200 mesh) in 7.5 M HNO_3 at 60°C was used for separation of the plutonium from the uranium. The volume of the resin in the chromatographic column was about 0.4 ml. The uranium fraction was recovered with 7.5 M HNO_3. For recovery of plutonium fraction 0.4 M HNO_3 was used. The volume of eluates in both cases did not exceed 10 ml. Chemical yield of plutonium was not less than 90%. The separation factor for plutonium from the uranium was about 10000. This level of decontamination was sufficient to exclude the influence of uranium on the mass spectrometric determination of plutonium isotopes with the exception of 238Pu. Therefore its determination was carried out with alpha-spectrometry after the separation 228Th. The content of 238Pu in molar fraction was 0.0711%.

8. Results of analysis of QS87

8.1. Determination of isotopic ratios

Results of analysis of QS87 ampoules 101 and 110 for uranium isotopic ratios are shown in Table 9. The measurements were carried out in according with the scheme on Fig. 4, 5. Besides in some cases the analysis of the uranium without the plutonium separation was carried out in order to estimate the influence of the plutonium presence. Results are given in Table 10.

Results in Tables 9 and 10 are obtained with use SRM U-500. It is interesting to compare these results with data obtained with use soviet SRM FCO 2702-83 and FCO 2704-83 (Tables 11 and 12).

The measurements and corrected isotopic ratios for plytonium in QS87 are shown in Table 13.

All data including double mixture are reviewed in Tables 14 and 15. The consideration of data shown in Tables 9-15 allows to conclude that there are good coincidences of major isotopic ratios:

- between the parallel loadings for one ampoule;
- between two ampoules A101 and A110;
- between the results obtained both for purified uranium and for uranium in the presence of plutonium;
- between the results normalized both with NBS U-500 and to FCO 2702-83 and 2704-83;
- between the results of analysis of double mixtures and QS87.

Speaking about 'minor' isotopic ratios it must be noted that the sample aliquoted from ampoule A101 was probably contaminated with 238U and 239Pu. So these results were not taken into consideration for the calculation of mean values. The increase of the ratio 239Pu/242Pu in QS87 in comparison with the double mixture can be explained by the presence 239Pu in initial material 233U (see item 2.1). On the other hand the noticeable decrese of the ratio 241Pu/242Pu in QS87 in comparison with the double mixture can be explained partly by the decay 241Pu since the time interval between the analysis of double mixture and QS787 is about 8 months. It gives rise to decrease the ratio 241Pu/242Pu about 2.3%.

8.2 Determination of element concentrations

The scheme of the measurements is given on Fig. 4-6. The weights of aliquots, results of the measurements and the calculation data are given in Tables 16, 17. The data of isotopic composition needed for calculation were taken from the Tables 9 and 13 (see the last lines).

Using the results of the determination of the concentration in double mixtures (Table 7) and the weight data for the preparation QS87 (item 6) it is possible to estimate the concentration values for both elements in QS87. These values were to be 1.02605 mg/g for the uranium and 6.5419 mkg/g for the plutonium. Within the confidence limits these values coincides with the data given in Table 17.

8.3. Final results obtained by RI

The characteristics of QS87 derived from the results obtained by RI according to the scheme on Fig. 4-6 are given in Tables 18, 19. In this report there is no analysis of the error sources but it is necessary to say that the main component of the total error of the *'major'* isotopic ratios is the error of certification of SRM's which were used for normalization.
The impurity contents in QS87 are given in Table 20

CONCLUSIONS

The preparation and analysis of the uranium and plutonium mixture for reference material QS87 has been achieved.

It were prepared 2 l of solution which was distributed into 20 ampoules had been transmitted to IAEA.

It is expedient to carry out the final certification on the basis of the results obtained in SAL and other network laboratories.

LITERATURE

I. Мельников Н.Н., Горохов И.М. Метод двойного изотопного разбавления. I. Теоретические основы. - в кн.: Развитие и применение методов ядерной геохронологии. Л., Наука, 1976, с. 7-27.

The Scheme of Analysis of Uranium Solution

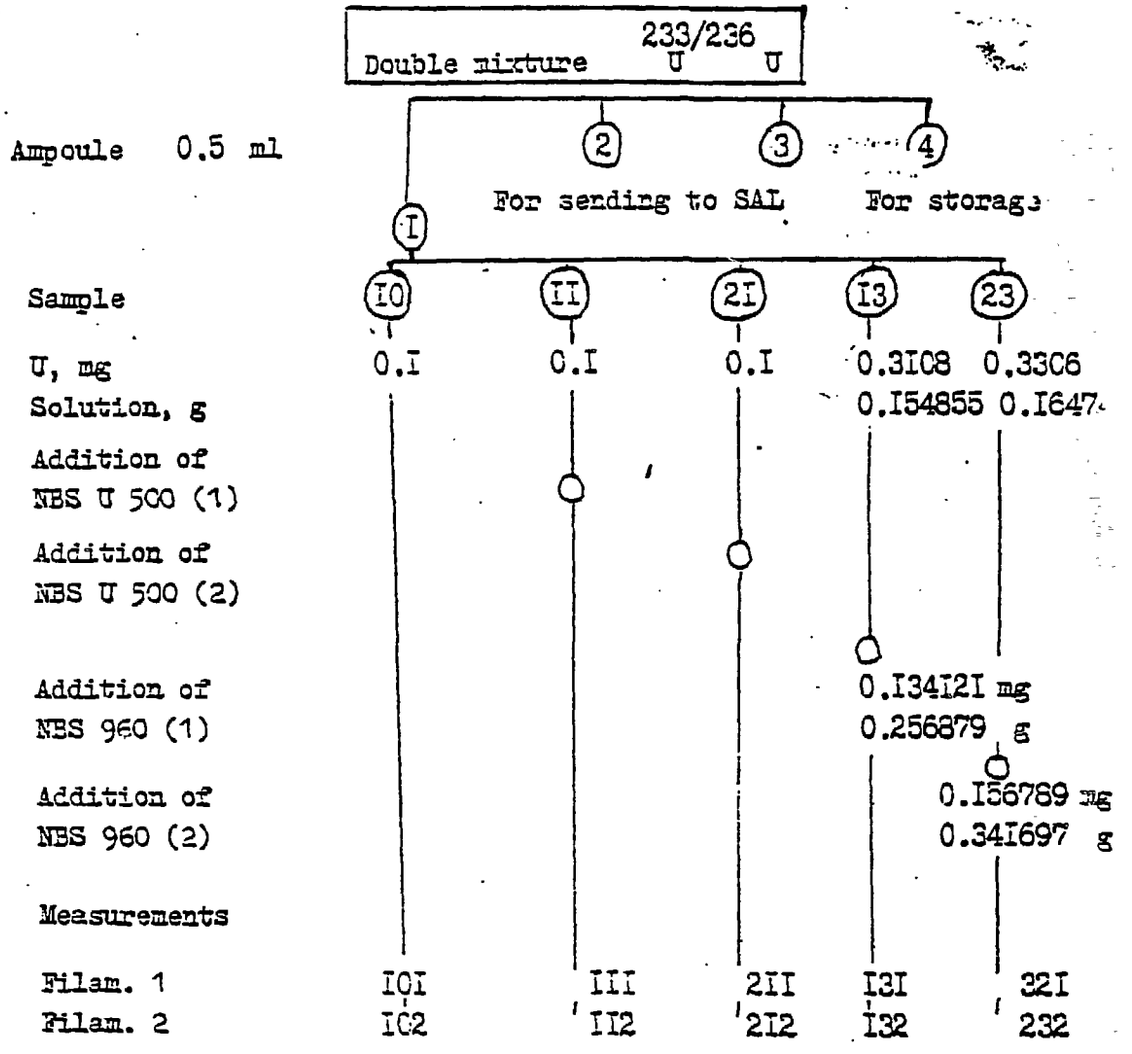

Fig. 1

The Scheme of Analysis of Plutonium Solution

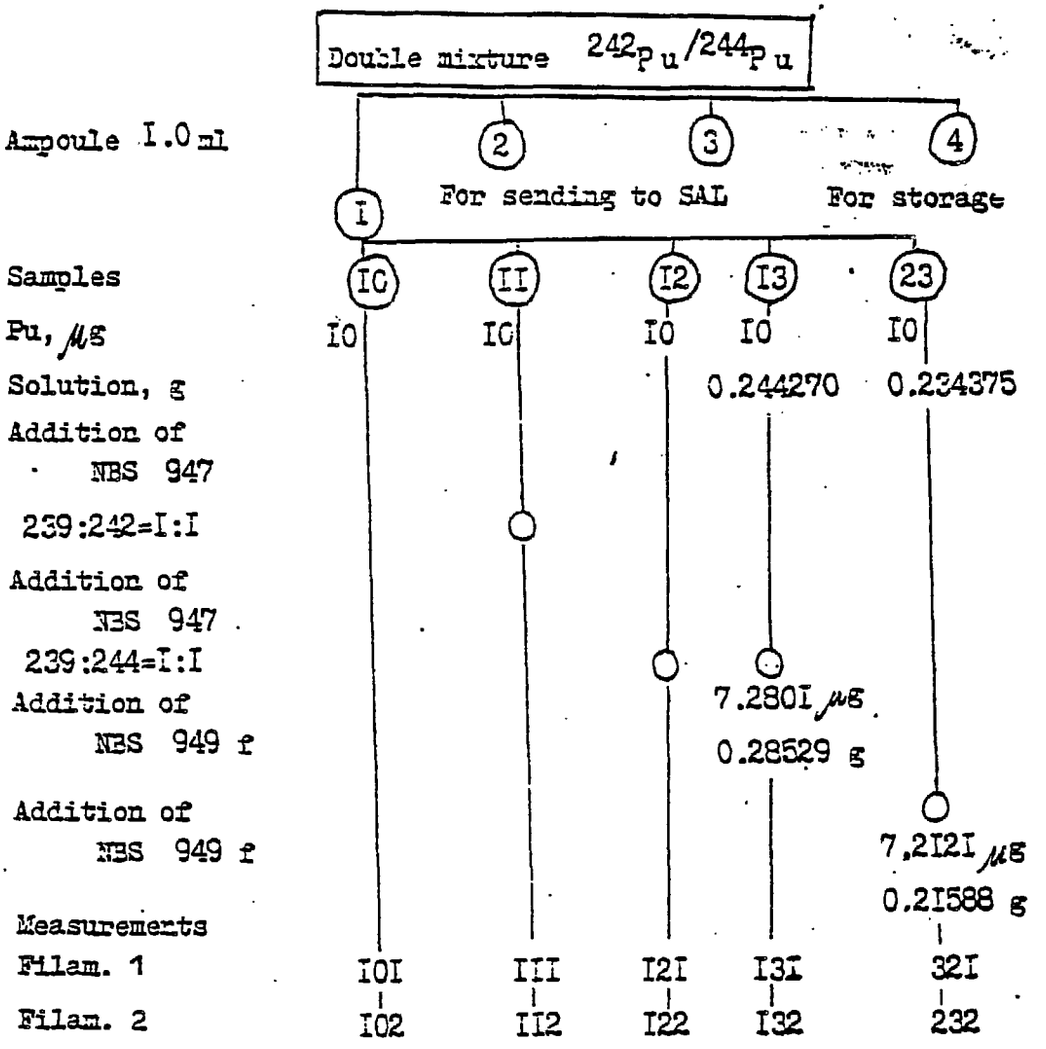

FIG. 2

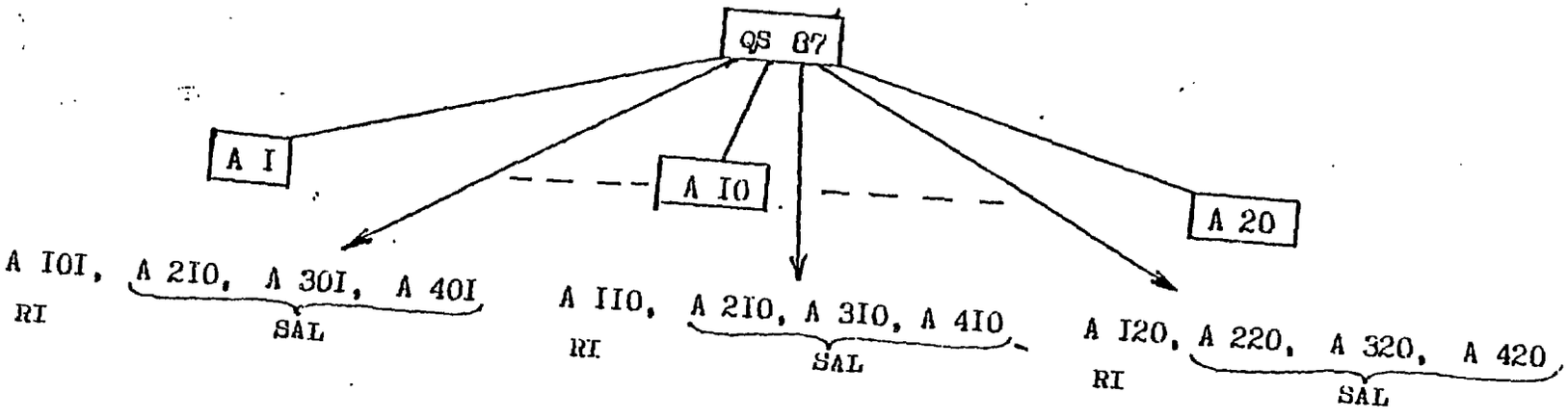

Fig. 3. The Scheme of Aliquating QS 87

Analytical scheme - RI

A 101

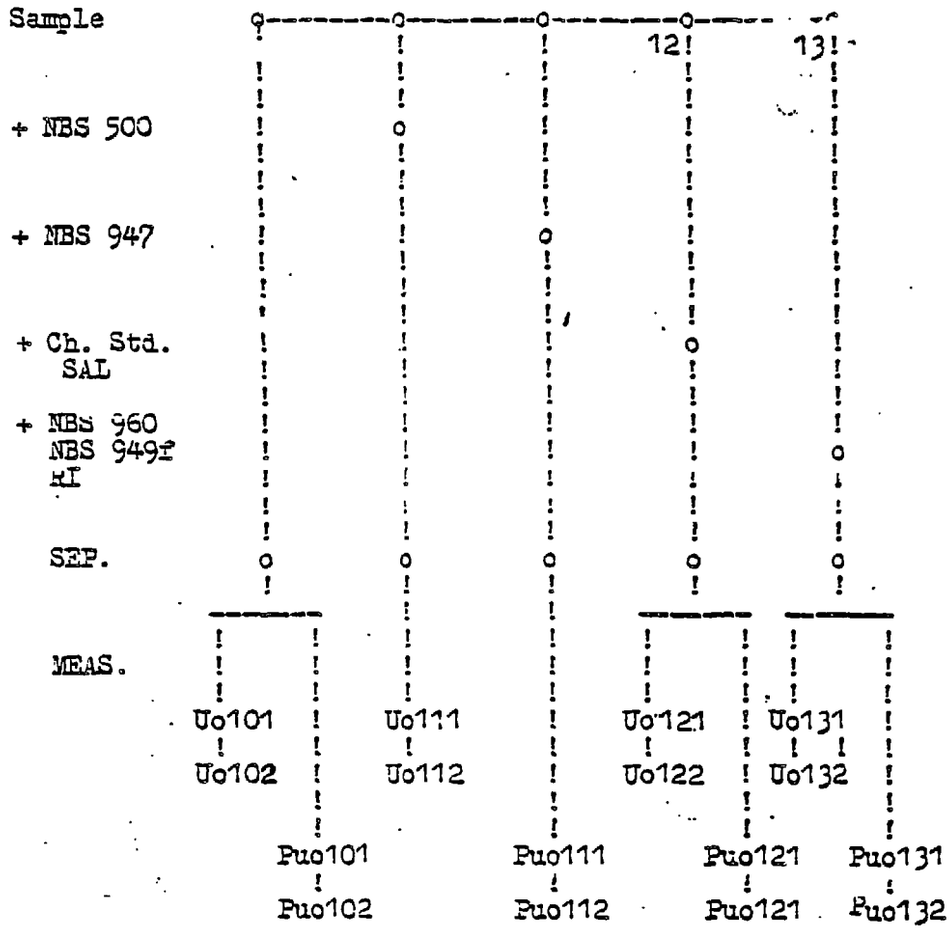

Fig. 4

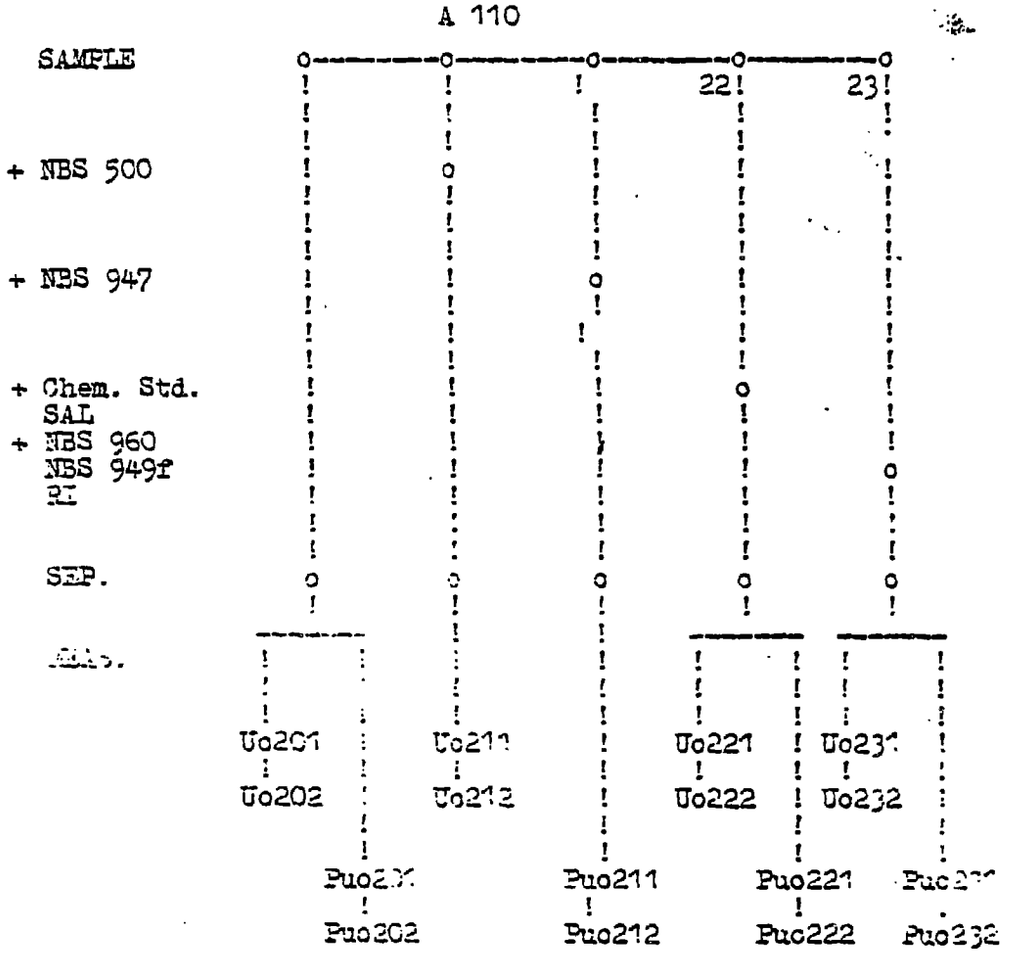

Fig. 5. Analytical Scheme RI

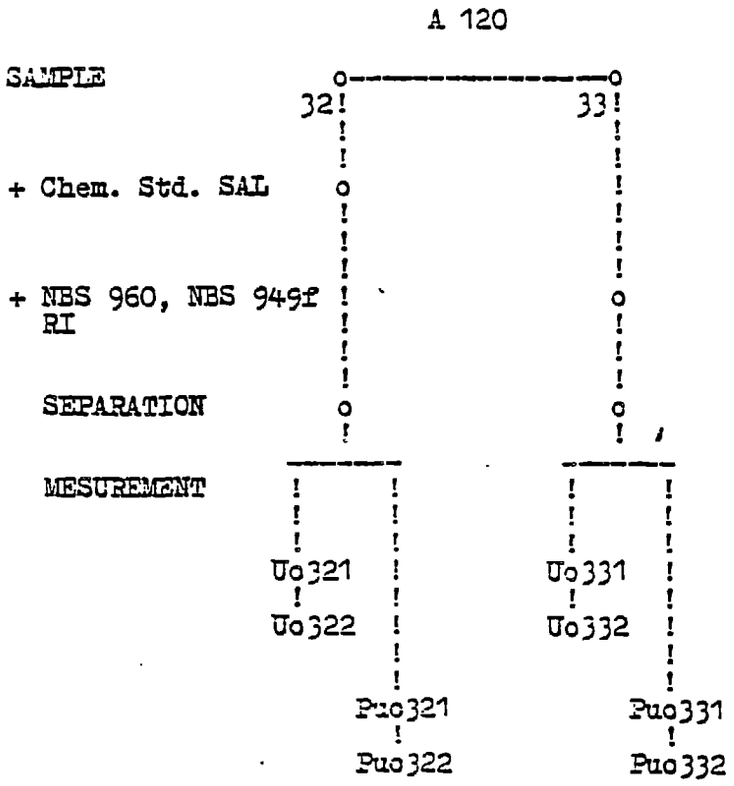

Fig. 6. Analytical Scheme RI

Table 1

Composition of the Uranium Starting Materials (atomic %)

Isotope	233	234	235	236	238
ГСО 3213-85 solution	± 97.201 0.002	± 2.655 0.002	± 0.0882 0.0003	± 0.0017 0.0001	± 0.0531 0.0005
$^{236}U_3O_8$	-	-	± 0.0045 0.0004	± 99.974 0.002	± 0.0218 0.0004

Table 2

Composition of the Plutonium Starting Materials (atomic %)

Isotope	238	239	240	241	242	244
СОП 009-87П	±0.097 0.005	± 0.035 0.003	±4.057 0.012	± 0.155 0.006	± 94.647 0.015	± 1.010 0.005
NBS 996	±0.005 0.001	±0.034 0.001	±0.677 0.004	±0.092 0.002	±1.325 0.004	±97.867 0.008

Table 3

Results of Measur ements of Isotopic Ratios in Uranium Double Mixture

Sample	I0I	I02	III	II2	2II	2I2	I3I	I32	23I	232
233/236	I.0I689	I.0I697	I.0I526	I.0I508	I.0I485	I.0I520	I.0I732	I.0I746	I.0I759	I.0I73
SD	0.00016	0.00044	0.00014	0.00030	0.00004	0.00022	0.00020	0.0007	0.00024	0.0002
235/236	9.65 10^{-4}	9.66 10^{-4}	I.33807	I.33795	I.5502	I.54948				
SD	0.04 10^{-4}	0.02 10^{-4}	0.00012	0.00015	0.0008	0.00015				
238/236	8.46 10^{-4}	8.49 10^{-4}	I.3384I	I.33840	I.5503	I.5494	0.86453	0.86445	0.94945	0.9494
SD	0.03 10^{-4}	0.02 10^{-4}	0.00013	0.00019	0.0005	0.0009	0.00003	0.00038	0.00006	0.0002
Number of series	5	5	8	4	5	5	5	5	5	5

Table 4

Results of Measurements of Isotopic Ratios in Plutonium Double Mixture

Sample	I0I	I02	III	II2	I2I	I22	I3I	I32	23I	232
244/242	0.39026	0.38979	0.38636	0.38604	0.38328	0.38396	0.390I5	0.39027	0.390I8	0.39062
SD	0.000I4	0,00020	0.000I7	0.00005	0.00020	0.00004	0.00025	0.00020	0.000I8	0.0004
240/242	0.045326	0.045234	0.20I98	0.20I75	0.3099I	0.30950				
SD	0,0000I8	0.00007	0.000I5	0.00020	0.000I8	0.00003				
239/242	$4.92 \cdot I0^{-4}$	$4.90 \cdot I0^{-4}$	0.65I78	0.65II5	I.I0083	I.09825	I.II765	I.II737	I.I5332	I.I50I7
SD	$0,04 \cdot I0^{-4}$	$0.04 \cdot I0^{-4}$	0.0006	0.0004	0.0006	0.00024	0.00I4	0.00I0	0.0008	0.0019
Number of series	4	4	5	3	5	5	5	5	5	4

Table 5

The Initial Data and Results of Calculation for Uranium Double Mixture

Ratio		233/236	234/236	235/236	238/236
R_t		0	not used	658.2252	658.4238
$\bar{R}_n^{\infty}$		I.0I726	0.027757	$9.655\ I0^{-4}$	$8.475\ I0^{-4}$
R_m^{∞}	III	I.0I526	not used	I.33807	I.3384I
	II2	I.0I508		I.33795	I.33840
	2II	I.0I485		I.5502	I.5503
	2I2	I.0I520		I.54948	I.5494
R_n IC	III	I.0I737	0.027759	$9.655\ I0^{-4}$ [6/]	$8.474\ I0^{-4}$
	II2	I.0I727	0.027757	$9.655\ I0^{-4}$	$8.475\ I0^{-4}$
	2II	I.0I708	0.027754	$9.654\ I0^{-4}$	$8.476\ I0^{-4}$
	2I2	I.0I73I	0.027758	$9.655\ I0^{-4}$	$8.475\ I0^{-4}$
$\bar{R}_n$ IC		I.0I726	0.027757	$9.655\ I0^{-4}$	$8.475\ I0^{-4}$
SD		0.000I2			

Table 6

The Initial Data and Results of Calculation for Plutonium Double Mixture

87-03-30

Ratio	238/242	239/242	240/242	241/242	244/242
R_t	not used	64.12346	15.47415	not used	0
$\bar{R}_n^{*}$	0.001028	0.000491	0.04528	0.001890	0.39021
R_m^{*} III	not used	0.65178	0.20198	not used	0.38636
II3		0.65115	0.20175		0.38604
I21		1.10083	0.30991		0.38328
I22		1.09825	0.30950		0.38396
R_n IC III	0.001028	0.000491	0.04527	0.001890	0.39031
II2	0.001026	0.000491	0.04524	0.001889	0.39055
I21	0.001027	0.000491	0.04526	0.001890	0.39042
I22	0.001028	0.000491	0.04527	0.001890	0.39028
$\bar{R}_n$ IC	0.001027	0.000491	0.04526	0.001890	0.39039
SD 88-06-01	0.001018		0.04525	1787	0.00013
Correct,	0.9908	0.99397	0.99955	0.9452	

87-03-30 12
88-06-01 2
14
12
1.17

12

Table 7

The Concentrations of Uranium and Plutonium in Double Mixture

Sample	U, mg/g	Pu, μg/g
I3I	2.00759	37.859
I32	2.00759	37.85I
23I	2.008I3	37.875
232	2.00842	37.9I5
Mean	2.00793	37.875
SD	0.0004I	0.028

Table 8

The Results of Analysis for Double Mixtures

	SAL	RI	SEALN	Mea...
233/236	I.0I759	I.0I726	I.0I733	I.0I739
234/236	0.027741	0.027757	0.027689	0.027729
235/236	0.00I007	0.000966	0.000984	0.000986
238/236	0.00I759*)	0.000848	0.000871	0.000860
Concentration of uranium, mg/g	2.0I50	2.0079	I.9807	
238/242	0.00II79*)	0.00I027	0.00I0I	0.00I02
239/242	0.000736*)	0.000491	0.000505	0.000498
240/242	0.045342	0.045260	0.045230	0.045277
241/242	0.00I897	0.00I890	0.00I98*)	0.00I894
244/242	0.390270	0.39039	0.390314	0.39032
Concentration of plutonium µg/g	37.853	37.875	37.656	

*) The results were not used for calculations of means.

Table 9

The Measured (R^{M}) and Internally Corrected Ratios for Uranium for QS 37

Ratio	233/236	234/236	235/236	238/236
A 101				
R_n^M 101	1.01769	0.027798	0.000969	0.000976
102	1.02153	0.027856	0.000968	0.000973
$R_n^{M'}$	1.01961	0.027827	0.000969	0.000975
R_m^M 111	1.01627	0.034735	0.67294	0.67340
112	1.01848	0.034894	0.67314	0.67212
R_n IC 111	1.01769	0.02779	0.000968	0.000976
112	1.01765	0.02779	0.000968	0.000976*)
A 110				
R_n^M 201	1.01996	0.027854	0.000969	0.000798
202	1.01964	0.027778	0.000963	0.000792
$R_n^{M'}$	1.01980	0.027816	0.000966	0.000795
R_m^M 211	1.01709	0.035044	0.70708	0.70666
212	1.01747	0.035066	0.70736	0.70673
R_n IC 211	1.01753	0.02777	0.000965	0.000796
212	1.01759	0.02778	0.000965	0.000796
$\bar{R}_n$ IC	1,01762	0,02778	0,000967	0,000796
SD	0,00007			

*) Not used for calculation of $\bar{R}_n$ IC.

Table 10

The Measured (R^M) and Internally Corrected (R_n IC) Ratios for Uranium for QS 87 without Separation from Plutonium.

Ratio		233/236	234/236	235/236	238/236
R_n^M	A IOI	I.0I96I	0.027827	0.000969	0.000975
R_m^M	III	I.0I553	0.034762	0.67400	0.67452
	II2	I.0I569	0.034662	0.67403	0.67450
R_n IC	III	I.0I703	0.027780	0.000968	0.000977
	II2	I.0I7I2	0.027782	0.000968	0.000977 x)
R_n^M	A IIO	I.0I980	0.027816	0.000966	0.000795
R_m^M	2II	I.0I593	0.034364	0.64639	0.64690
	2I2	I.0I802	0.034516	0.64681	0.64574
R_n IC	2II	I.0I769	0.027778	0.000965	0.000796
	2I2	I.0I729	0.027770	0.000965	0.000796
$\bar{R}_n$ IC		I.0I728	0.02778	0.000967	0.000796
SD		0.00019			

Table 11

The Characteristics of the Uranium Isotopic Standard Reference Materials (at. %)

Isotop	234	235	236	238	235/238
ГСО 2702-83	$\pm$0.367 $\pm$0.002	$\pm$ 49.568 $\pm$ 0.0I2	$\pm$0.4569 $\pm$0.0005	$\pm$49.588 $\pm$ 0.0I2	$\pm$ I.0000 $\pm$ 0.0005
ГСО 2704-83	$\pm$0.96I $\pm$0.004	$\pm$89.868 $\pm$ 0.005	$\pm$0.2698 $\pm$0.0005	$\pm$8.90I $\pm$0.004	$\pm$I0.097 $\pm$.0.005

Table 12

The Measured ($R^{\pm}$) and Internally Corrected (R_n IC) Ratios of Uranium for QS 87 with Using SRM "ГСО"

Ratio	233/236	234/236	235/236	238/236
$R_n^{\pm}$	I.0I723	0.0278I3	0.000960	0.000782
$R_m^{\pm}$ +2702	I.0II33	0.033022	0.02I55	0.72I00
+2704	I.0II45	0.043497	I.48820	0.I4835
R_nIC +2702	I.0I756	0.0278I9	0.000960	0.000782
+2704	I.0I782	0.027824	0.000960	0.000782
$\bar{R}_n$ IC	I.0I769	0.027822	0.000960	0.000782

Table 13

The Measured (R^{M}) and Internally Corrected (R_n IC) Ratios of Plutonium for QS 37

Ratio		239/242	240/242	241/242	244/242
A 101					
R_p^M	101	0.000835	0.045338	0.001820	0.30989
	102	0.000796	0.045244	0.001766	0.38997
$R_p^{M'}$		0.000816	0.045291	0.001793	0.38993
R_m^M	111	1.17570	0.32784	0.034235	0.38277
	112	1.17449	0.32760	0.033993	0.38298
R_n IC	111	0.000815	0.04525	0.001792	0.39027
	112	0.000815[x]	0.04525	0.001792	0.39028
A 110					
R_p^M	201	0.000640	0.045249	0.001810	0.38962
	202	0.000640	0.045174	0.001815	0.39006
$R_p^{M'}$		0.000640	0.045212	0.001813	0.38984
R_m^M	211	1.04528	0.29657	0.030806	0.38418
	212	1.04622	0.29679	0.030419	0.38396
R_n IC	211	0.000639	0.04516	0.001812	0.39025
	212	0.000639	0.04518	0.001812	0.39013
$\bar{R}_n$ IC		0.000639	0.04521	0.001802	0.39023
SD					0.00007

[x]) Not used for calculation $\bar{R}_n$ IC .

Table 14

The Internally Corrected Ratios for Uranium Measured under Various Conditions

The conditions of the analysis	Number of meas.	233/236	234/236	235/236	238/236
Double mixture (mean from 3 lab., tab.8)	3	I.0I739	0.02773	0.000986	0.000860
QS 87 (tab.9)	2	I.0I762	0.02778	0.000967	0.000796
QS 87 without separation from Pu (tab. 10)	2	I.0I728	0.02778	0.000967	0.000796
QS 87 by use FCO (tab. 12)	2	I.0I769	0.02782	0.000960	0.000782

Table 15

The Internally Corrected Ratios of Plutonium for Double Mixture and QS 87

	Number of samples	238/242	239/242	240/242	24I/242	244/242
Double mixture (Table 8)	3	0.00I02	0.000498	0.045277	0.00I894	0.39C
QS 87 (Tab.I3)	2	0.00I03*)	0.000639	0.0452II	0.00I802	0.39C

*) α -spectrometry .

Table 16

The Chacteristics of Solutions for Determination of Concentration of Uranium and Plutonium for QS 87

Sample	Weight, g	SRM used	Weight of SRM, g	Concentration of SRM U, mg/g ; Pu , μg/g
I2	0.94384	CL 87-I9	0.6399I	
I3	0.77786	RI NBS 960	0.52I65	0.6883I3
		NBS 949	0.I25I6	25.53I5
22	0.83659	CL 87-20	0.67066	
23	0.92027	RI NBS 960	0.72I48	0.6883I3
		NBS 949	0.I6749	25.53I5
32	0.93478	CL 87-2I	0.66085	
33	0.94362	RI NBS 960*)	0.90462	0.44I42
		NBS 949	0.I5946	25.5352

*) Other sample of NBS 960 was used.

Table 17

The Concentration of Uranium and Plutonium in QS 787

Date	Sample	233/236	238/236	IC conc. of U, mg/g	239/242	244/242	IC conc. of Pu, µg/g
	A I0I						
	I2I	I.020I8	I.II369		I.0I320	0.39015	
I0.I987	I22	I.02089	I.II370		I.0II74	0.3903I	
	I3I	I.0I707	0.90I89	I.026II	0.89327	0.38952	6.5424
	I32	I.0I774	0.90I69	I.02509	0.89359	0.38960	6.5380
	A II0						
	22I	I.0I860	I.3I684		I.I9522	0.39074	
I0.I987	222	I.0I698	I.3I802		I.I9864	0.38976	
	23I	I.0I720	I.05333	I.02689	I.00928	0.38995	6.5382
	232	I.0I753	I.05400	I.0260I	I.00894	0.38999	6.5384
	A I20						
	32I	I.0I694	I.I6204		I.05274	0.39073	
0I.I988	322	I.020I7	I.I60I8		I.05047	0.39I09	
	33I	I.0I936	0.82567	I.02609	0.9382I	0.38996	6.53I6
	332	I.0I885	0.82556	I.02657	0.93773	0.3900I	6.5337
	Mean			I.02626			6.5372
	SD			0.0004			0.0039

Table 18

The Characteristics of QS 87 (Uranium)

Ratio	233/236	234/236	236/236	236/236	238/236
R_n	$\pm$1.01762 $\pm$0.0005	$\pm$ 0.02778 0.00003	$\pm$0.000967 $\pm$0.000010	I	$\pm$0.000796 $\pm$0.000010
Isotope	233	234	235	236	238
At. %	$\pm$49.709 $\pm$ 0.018	$\pm$1.3570 $\pm$0.0015	$\pm$0.0472 $\pm$0.0005	$\pm$48.848 $\pm$ 0.018	$\pm$0.0389 $\pm$0.0005
Concentration, mg/g	1.0263 $\pm$ 0.0006				

Table 19

The Characteristics of QS 87 (Plutonium)

Ratio	238/242	239/242	240/242	241/242	241/241	244/242
R_n	$\pm$0.00103 $\pm$0,00001	$\pm$0,000639 $\pm$0.000005	$\pm$0.04521 $\pm$0.00006	$\pm$0.001802 $\pm$0.000040	1	$\pm$0.39023 $\pm$0,00047
Isotope	238	239	240	241	242	244
At. %	$\pm$0.0716 $\pm$0.0004	$\pm$0.0444 $\pm$0.0003	$\pm$3.142 $\pm$0.005	$\pm$0,1252 $\pm$0.0029	$\pm$69.497 $\pm$ 0.06	$\pm$27.120 $\pm$ 0.023
Concentration, $\mu g/g$			$\pm$6.537 $\pm$0.006			

Table 20

Impurities, Expressed as Parts per Million, by Weight in QS 87 Solution Determined by Spectrographic Analysis

Al	Mn	Fe	Pb	Mg	Ca	Na	Si	B	K	Cr
1.4	0.8	1.7	0.13	0.27	1.5	4.3	42	0.4	0.71	0.16

ANNEX 4

Certificate of Analysis
of
SAL 9914 (QS 87)

INTERNATIONAL ATOMIC ENERGY AGENCY
AGENCE INTERNATIONALE DE L'ENERGIE ATOMIQUE
МЕЖДУНАРОДНОЕ АГЕНТСТВО ПО АТОМНОЙ ЭНЕРГИИ
ORGANISMO INTERNACIONAL DE ENERGIA ATOMICA

WAGRAMERSTRASSE 5, P.O. BOX 100, A-1400 VIENNA, AUSTRIA
TELEX: 1-12645, CABLE: INATOM VIENNA, FACSIMILE: 43 222 230184, TELEPHONE: (222) 2360

IN REPLY PLEASE REFER TO:
PRIERE DE RAPPELER LA REFERENCE:

DIAL DIRECTLY TO EXTENSION:
COMPOSER DIRECTEMENT LE NUMERO DE POSTE:

Certificate of Analysis
Spike Solution for Isotopic and Isotope Dilution Analysis of Uranium and Plutonium

SAL-9914 (QS 87)
(Revision 1)

The atomic isotopic ratios of this spike are equal to

$^{233}U/^{236}U = 1.0174 \pm 0.0011$
$^{234}U/^{236}U = 0.027775 \pm 0.000034$
$^{235}U/^{236}U = 0.000960 \pm 0.000033$
$^{238}U/^{236}U = 0.000791 \pm 0.000050$

$^{238}Pu/^{242}Pu = 0.001014 \pm 0.000016$
$^{239}Pu/^{242}Pu = 0.000562 \pm 0.000092$
$^{241}Pu/^{242}Pu = 0.001754 \pm 0.000026$
$^{244}Pu/^{242}Pu = 0.39033 \pm 0.00082$

This corresponds to the isotopic composition

Isotope	Atom %	Weight %
^{233}U	49.7043	49.3896
^{234}U	1.3569	1.3541
^{235}U	0.0469	0.0470
^{236}U	48.8533	49.1701
^{238}U	0.0386	0.0392
^{238}Pu	0.0705	0.0692
^{239}Pu	0.0389	0.0384
^{240}Pu	3.1413	3.1091
^{241}Pu	0.1219	0.1212
^{242}Pu	69.4998	69.3635
^{244}Pu	27.1276	27.2986

The atomic weight of the mixture is
U Atomic Wt = 234.5246
Pu Atomic Wt = 242.5346

The chemical concentrations of the major isotopes of the spike are
^{236}U = (504.42 ± 0.51) /ug/g ±0.51
^{242}Pu = (4.536 ± 0.015) /ug/g ±0.015

All above values are valid for 1988-06-01.

(1) The Spike SAL 9914 (QS87) is intended to be used for isotopic and/or isotope dilution analyses of uranium and plutonium with internal standard correction of mass fractionation effects.

(2) This material was prepared by the Khlopim Radium Institute in Leningrad.

(3) The composition quoted in this certificate is based on mass spectrometric analyses performed at the Khlopin Radium Institute in Leningrad (USSR), the Service d' Etudes Analytiques in the Centre d'Etudes Nucléaires de Saclay (France), the Bundesanstalt für Material Prüfung (West Berlin), and the Safeguards Analytical Laboratory of the International Atomic Energy Agency.

(4) These measurements were calibrated against NBS-500, FCO-2702-83, FCO-2704-83, NBS947, NBS960, MU1, NBS949 and MP1/EC 201 isotopic and chemical reference materials.

(5) The Confidence Limits were calculated by propagating the variances of the random errors of mass spectrometric measurements, chemical treatments and between laboratory effects as well as the common calibration errors. They are expressed for a 95% confidence level (2σ).

(6) The statistical evaluation of the measurements was performed by S. Deron and H. Aigner following a model derived by J. Jaech. It is described in the report SAL-IR/23/89 of October 1989.

(7) The calculations used the following physical constants

Isotope	Atomic Mass	Half life (in years)
^{233}U	233.03963	$(1.529\pm.002)\ 10^5$
^{234}U	234.04095	$(2.457\pm.003)\ 10^5$
^{235}U	235.04392	$(7.037\pm.007)\ 10^5$
^{236}U	236.04556	$(2.342\pm.001)\ 10^7$
^{238}U	238.05079	$(4.469\pm.001)\ 10^9$
^{238}Pu	238.04956	$(8.774\pm.009)\ 10^1$
^{239}Pu	239.05216	$(2.411\pm.003)\ 10^4$
^{240}Pu	240.05381	$(6.55\ \pm.02)\ 10^3$
^{241}Pu	241.05685	$(1.44\ \pm.02)\ 10^1$
^{242}Pu	242.05874	$(3.76\ \pm.02)\ 10^5$
^{244}Pu	244.06420	$(8.2\ \pm.1)\ 10^7$

Vienna, the 30 January 1990

S. Deron
Head, Safeguards
Analytical Laboratory
Agency's Laboratory

ANNEX 5

Results of IDMS Analyses of Spent Fuel Solutions using QS 87 as Spike and Internal Standard

Results of IDMS Analyses of Spent Fuel Solutions
using SAL-9914 (QS87) as Spike and Internal Standards

Series	Sample	Pu	U	Pu/U
2218	1	6.5991	689.89	0.95654
		6.6065	689.94	0.95755
2229	1	7.5564	803.72	0.94018
		7.5542	802.86	0.94091
	3	6.2276	690.07	0.902460
		6.2196	690.41	0.900778
2230	1	6.2164	679.03	0.91548
		6.2183	678.50	0.91648
	2	7.3909	790.47	0.935000
		7.3903	790.71	0.93464
	3	6.8647	788.68	0.87040
		6.8699	788.55	0.87121
	4	7.7875	876.06	0.88892
		7.7923	876.60	0.88892
	5	8.7213	939.47	0.92832
		8.7145	939.27	0.92779
2229	2	7.3730	835.02	0.88297
		7.3677	834.72	0.88266
2233	1	6.8200	745.33	0.91503
		6.8213	745.83	0.91459
	2	6.6591	729.86	0.91238
		6.6671	730.84	0.91225
2252	1	6.7189	753.15	0.89211
		6.7226	753.38	0.89233
	2	7.1345	771.67	0.92455
		7.1330	771.67	0.92436
2254	1	5.9481	640.69	0.92839
		5.9470	640.61	0.92833
	2	6.8300	709.27	0.96296
		6.8292	709.64	0.96235
	3	6.9731	772.05	0.90319
		6.9797	772.67	0.90332

Series	Sample	Pu	U	Pu/U
2255	1	6.2549	686.17	0.91157
		6.2561	686.47	0.91134
2256	1	6.9530	806.73	0.86187
		6.9524	806.57	0.86197
	3	6.9788	775.25	0.90020
		6.9832	775.69	0.90026
	4	6.6076	707.82	0.93351
		6.6099	707.87	0.93377
2256	2	22.811	0.220499	102.452
		22.843	0.220450	103.620
2259	1	5.7807	593.17	0.97454
		5.7756	592.60	0.97462
2260	1	6.8506	407.26	1.68212
		6.8497	407.27	1.68186
	2	6.0196	710.08	0.84774
		6.0121	708.84	0.84816
2262	1	7.1564	763.59	0.93720
		7.1657	764.29	0.93756
2486	1	0.173902	12.3153	1.41208
		0.173868	12.3164	1.41168
2571	1	9.4453	0.100198	0.94266
		9.4628	0.100288	0.94356
	2	9.7334	0.102224	0.95216
		9.7531	0.102348	0.95294
	3	8.2461	859.66	0.95923
		8.2405	859.18	0.95011
	4	2.3685	250.97	0.94374
		2.3669	250.81	0.94371
Intraclass Coeff. variation		0.062%	0.049%	0.047%

Define the following coefficients of variation

U measurement error:	SIU
Pu measurement error:	SIP
Sample treatment error:	ST
Pu/U measurement error:	SPU
U analysis error:	SU
Pu analysis error:	SP

The following relationships applies

$$SU^2 = SIU^2 + ST^2 = 0.049^2$$
$$SP^2 = SIP^2 + ST^2 = 0.062^2$$
$$SPU^2 = SUY^2 + SIP^2 = 0.047^2$$

Thus

$$ST = 1/2 \left[SU^2 + SP^2 - SPU^2\right]^{1/2} = 0.045\%$$
$$SIU = \left[SU^2 - ST^2\ 1/2\right] = 0.019\%$$
$$SIP = \left[SP^2 - ST^2\ 1/2\right] = 0.043\%$$

ANNEX 6

Analysis of Variance and Propagation of Errors used for the Certification of QS 87

(J. Jaech)

Model:

μ = true value
A_i = deviation from μ for lab (or method) i; i = 1, 2, ...R
$B_{j(i)}$ = deviation from μ for sample (or treatment) j within lab i; j = 1, 2, ..., L_i
$C_{k(ij)}$ = deviation from μ for measurement k within sample j within lab i; k = 1, 2,....., N_{ij}

$$X_{ijk} = \mu + A_i + B_{j(i)} + C_{k(ij)}$$

How to estimate J_A^2, J_B^2, J_C^2:

Solve the 3 estimating equations

$$M_A = J_C^2 + P_1 J_B^2 + R_1 J_A^2$$

$$M_B = J_C^2 + P_2 J_B^2$$

$$M_C = J_C^2$$

where $N_i = \sum_j N_{ij}$ $\qquad N = \sum_i N_i$

$$F_A = R - 1$$

$$F_B = \sum_i L_i - R$$

$$F_C = \sum_{ij} N_{ij} - \sum_i L_i$$

$$T_{ij} = \sum_k X_{ijk} \qquad S_0 = T^2/N$$

$$T_i = \sum_j T_{ij} \qquad S_1 = \Sigma_i T_i^2/N_i$$

$$T = \sum_i T_i \qquad S_2 = \sum_{ij} T_{ij}^2/N_{ij}$$

$$S_3 = \sum_{ijk} X_{ijk}^2$$

$$S_A = S_1 - A_0 \qquad M_A = S_A/F_A$$

$$S_B = S_3 - S_2 \qquad M_B = S_B/F_B$$

$$S_C = S_3 - S_2 \qquad M_C = S_C/F_C$$

$$G_i = (1/N_i - 1/N)/F_A$$
$$G_{ij} = (1/N_{ij} - 1/N_i)/F_B$$

$$P_1 = \sum_{ij} N_{ij}^2 G_i$$

$$P_2 = \sum_{ij} N_{ij}^2 G_{ij}$$

$$R_1 = \sum_i N_i^2 G_i$$

$$\text{Lab Mean} = \bar{\bar{X}}_i = \frac{\sum_{ij} X_{ijk}}{N_i} = \frac{T_i}{N_i}$$

$$\text{Best estimate} = \bar{\bar{X}} = \frac{\sum_i W_i \bar{\bar{X}}_i}{\sum_i W_i}$$

$$\bar{\bar{X}}_i = \mu + A_i + \frac{\sum_{j=1}^{L_i} N_{ij} B_{j(i)}}{N_i} + \frac{\sum_{jk} C_{k(ij)}}{N_i}$$

Example: (% Recovery - 100 NBS 949/d)

Lab	1	2	2	3	3	4	4	5	5	6
Sample	1	1	2	1	2	1	2	1	2	1
Meas	.03	.09	.45	-.10	-.18	.02	-.08	.06	.26	.09
	.10	.21	.23	-.05	-.21	-.10	-.10	.20	.14	-.06
	-.10	.09	.08	-.12	-.17	-.04	.01	.23	.31	-.10
	-.08			-.01	-.23	.00	-.09	.07		.02
				-.07	-.19	-.03	-.07			.04
						-.04	.01			

$R = 6$

$L_1 = 1$, $L_2 = 2$, $L_3 = 2$, $L_4 = 2$

$N_{11} = 4$, $N_{21} = 3$, $N_{22} = 3$, $N_{31} = 5$, $N_{32} = 5$

$N_{51} = 4$, $N_{52} = 3$, $N_{61} = 5$

$N_1 = 4$, $N_2 = 6$, $N_3 = 10$, $N_4 = 12$, $N_5 = 7$, $N_6 = 5$

$N = 44$

$F_A = 5$

$F_B = 10-6 = 4$

$F_C = 44-10 = 34$

$T_{11} = -.05$, $T_{21} = .39$, $T_{22} = .76$, $T_{31} = -.35$, $T_{32} = -.98$, $T_{41} = -.19$, $T_{42} = -.32$

$T_{51} = .56$, $T_{52} = .71$, $T_{61} = -.01$

$T_1 = -.05$, $T_2 = 1.15$, $T_3 = -1.33$, $T_4 = -.51$, $T_5 = 1.27$, $T_6 = -.01$

$T = 0.52$

$S_0 = 0.006145$

$S_1 = 0.650041$

$S_2 = 0.729975$

$S_3 = 0.928200$

$S_A = 0.643896$, $M_A = 0.128779$

$S_B = 0.079934$, $M_B = 0.019984$

$S_C = 0.198225$, $M_C = 0.005830$

$G_1 = 0.045455$, $G_2 = 0.028788$, $G_3 = 0.015455$, $G_4 = 0.012121$, $G_5 = 0.024026$, $G_6 = 0.035455$

$G_{11} = 0$, $G_{21} = 0.041667$, $G_{22} = 0.041667$, $G_{31} = 0.025$, $G_{32} = 0.025$, $G_{41} = 0.020833$, $G_{42} = 0.020833$

$G_{51} = 0.026786$

$G_{52} = 0.047619$

$G_{61} = 0$

$P_1 = 3.6507$ $\qquad 0.128779 = \sigma_C^2 + 3.6507\ \sigma_B^2 + 7.1182\ \sigma_A^2$

$P_2 = 4.3571$ $\qquad 0.019984 = \sigma_C^2 + 4.3571\ \sigma_B^2$

$\qquad 0.005830 = \sigma_C^2$

$R_1 = 7.1182$

$\qquad \sigma_C^2 = 0.005830$

$\qquad \sigma_C^2 = 0.003248$

$\qquad \sigma_C^2 = 0.015607$

$\bar{\bar{X}}_1 = -0.0125$ $\qquad \sigma^2_{\bar{\bar{X}}_1} = \sigma_A^2 + \sigma_B^2 + \frac{\sigma_C^2}{4} = 0.020313$

$\bar{\bar{X}}_2 = 0.1917$ $\qquad \sigma^2_{\bar{\bar{X}}_2} = \sigma_A^2 + \frac{18}{36} + \sigma_B^2 + \frac{\sigma_C^2}{6} = 0.018203$

$\bar{\bar{X}}_3 = -0.1330$ $\qquad \sigma^2_{\bar{\bar{X}}_3} = \sigma_A^2 + \frac{50}{100}\ \sigma_B^2 + \frac{\sigma_C^2}{10} = 0.017814$

$\bar{\bar{X}}_4 = -0.0425$ $\qquad \sigma^2_{\bar{\bar{X}}_4} = \sigma_A^2 + \frac{72}{144}\ \sigma_B^2 + \frac{\sigma_C^2}{12} = 0.017717$

$\bar{\bar{X}}_5 = 0.1814$ $\qquad \sigma^2_{\bar{\bar{X}}_5} = \sigma_A^2 + \frac{25}{49}\ \sigma_B^2 + \frac{\sigma_C^2}{07} = 0.018097$

$\bar{\bar{X}}_6 = -0.0020$ $\qquad \sigma^2_{\bar{\bar{X}}_6} = s_A^2 + s_B^2 + \frac{\sigma_C^2}{5} = 0.020021$

$$\bar{\bar{\bar{X}}} = \frac{(49.23)(-.0125) + ... + (49.95)(-.0020)}{321.96} = 0.0310$$

$$\sigma^2_{\bar{\bar{\bar{x}}}} = (321.96)^{-1} = 0.003106$$

$$\sigma^2_{\bar{\bar{\bar{x}}}} = 0.0557$$

$W_1 = 49.23$
$W_2 = 54.94$
$W_3 = 56.14$
$W_4 = 56.44$
$W_5 = 55.26$
$W_6 = \underline{49.95}$
$\quad 321.96$

Weighted Means
And Degrees Of Freedom

$$\bar{\bar{x}} = \frac{\sum_i w_i \bar{x}_i}{\sum_i w_i}$$

$$w_i = \frac{1}{S_i^2}$$

$$S_i^2 = S_A^2 + S_B^2 \frac{\sum_j N_{ij}^2}{N_i^2} + \frac{S_C^2}{N_i}$$

$$S^2 = \gamma_A S_A^2 + \gamma_B S_B^2 + \gamma_C S_C^2 = \frac{1}{\sum_i w_i}$$

$$\gamma_A = \frac{\sum_i w_i^2}{(\sum_i w_i)^2}$$

$$\gamma_B = \frac{\sum_i \{w_i^2 (\sum_j N_{ij}^2 / N_i^2)\}}{(\sum w_i)^2}$$

$$\gamma_C = \frac{\sum_i (w_i^2 / N_i)}{(\sum w_i)^2}$$

If S_A^2, S_B^2 have negative estimates, set S_A or S_B = o

$$DF = \frac{\left(\sum_l a_l S_l^2\right)^2}{\sum_l \frac{a_l^2 S_l^4}{DF_l}}$$

(l = A, B, C)