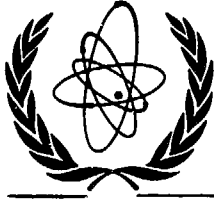


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THE SAFEGUARDS ANALYTICAL LABORATORY (SAL)
IN THE
AGENCY'S SAFEGUARDS MEASUREMENT SYSTEM
ACTIVITY IN 1990

by

G. Bagliano, J. Cappis, S. Deron, J.L. Parus

Safeguards Analytical Laboratory
International Atomic Energy Agency
Seibersdorf, Austria

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Safeguards Analytical Laboratory
IAEA, A-2444 Seibersdorf

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1. Introduction

The IAEA applies Safeguards at the request of a Member State to whole (1) or part (2) of its nuclear materials. The Agency and the State conclude for this purpose a Safeguards Agreement with the objective to demonstrate that the materials put under IAEA Safeguards are used solely for peaceful purposes. In 1990 the Agency was safeguarding nuclear materials at about 910 facilities in 57 different states. This meant in particular safeguarding about 12 tons of high enriched uranium (HEU) (+8% more than in 1989), 20 tons of separated plutonium outside reactor areas (+48%), in addition to about 35500 tons of low enriched uranium (LEU) (+5%) and 62000 tons of source materials (+9%) (3). The verification of nuclear material accountability still constitutes the fundamental method of control, although sealing and surveillance procedures play an important complementary and increasing role in Safeguards.

Accountability verifications involve independent measurements and analyses according to randomized sampling plans. The inspectors can nowadays do most of the necessary analyses directly at the plant using Non Destructive Assay (NDA) techniques or Installed Instrumentation (II) so that the absence of abrupt diversions can be verified in a timely fashion and anomalies may be resolved on the spot. However a small fraction of samples must still be analyzed at independent analytical laboratories using conventional Destructive Analytical (DA) methods of highest accuracy in order to verify that small potential biases in the declarations of the State are not masking protracted diversions of significant quantities of fissile materials. The results of these off-site analyses are used to verify once a year the closing of the material balance and the amount of Material Unaccounted For (4).

Off-site DA are also needed to characterize the working reference materials required for the calibration, the quality control and the testing of the Agency's on-site measurements methods. Off-site DA measurements are also used to verify the quality of the operator's measurements system.

The SAL is operated by the Agency's Laboratories at Seibersdorf to provide to the Department of Safeguards and its inspectors such off-site Analytical Services, in collaboration with the Network of Analytical Laboratories (NWAL) of the Agency (5).

The services of DA in the Agency's Safeguards measurement system are coordinated by the Director of the Division of Development and Technical Support (SGDE) assisted by a steering committee of which both the Head of SAL and the Head of the Chemical Analysis Unit of SAL are active members; the organization, the resources and the functions of the off-site DA system are described elsewhere (5, 6, 7, 8).

The efforts of the DA Services are traditionally to reduce the time required for the shipment of the samples and for their analyses. The conditioning, which the samples must undergo before they can be shipped to SAL, must also be simplified or automatized so that witnessing of these operations by the inspector becomes simpler and more effective.

In the last years SAL and the Safeguards DA Services have become more directly involved in the qualification and utilization of on-site analytical instrumentation such as K-edge X-Ray absorptiometers and quadrupole mass spectrometers.

New large bulk handling facilities with plutonium throughputs of up to 8 tons/year, which are coming in operation and will come under safeguards in the nineties, present a new challenge to Agency's Safeguards. For the Off-Site DA Services this will require, if ever possible, improving in particular by a factor 5 to 10 at such plants the accuracy of the analyses of feed and products. On-Site analyses of the same materials will also have to be done at the plants with accuracies of 0.1-0.2% in order to enable the timely detection of small accountancy differences which would within a month accumulate to Safeguards significant amounts. The Safeguards DA Services are requested to advise on the justification and feasibility of operating for this purpose a DA verification laboratory directly on the site, versus alternative approaches (9).

The nature and the origin of the samples analyzed, the measurements usually requested by the IAEA inspectors, the methods and the analytical techniques available at SAL and at the NWAL with the performances achieved during the past years are described and discussed in several documents (5, 7, 8, 10).

The Laboratories of NWAL are listed in Table 1 whereas the organizational chart of SAL is presented in Fig. 1. The two units of SAL always work in symbiosis sharing systematically the analytical workload required for each measured sample (7). Consequently all the activities undertaken at SAL are presented as being performed by one body.

This report gives an evaluation compared with 1989 of the volume and the quality of the analyses reported in 1990 by SAL and by the NWAL in reply to requests of IAEA Safeguards inspectors.

The reports summarizes also on-site DA developments and support provided by SAL to the Division of Safeguards Operation and special training courses to the IAEA Safeguards inspectors.

Table 1: Network Laboratories

Netherlands Energy Research Foundation, Petten, Netherlands
Harwell Laboratory, UK
Bundesanstalt für Materialprüfung, Berlin, Federal Republic of Germany
V.G. Khlopin Radium Institute, Leningrad (St Petersburg) USSR
Nuclear Research Institute, Rez, Czechoslovakia
Zentralinstitut für Kernforschung, Rossendorf, Federal Republic of Germany
Service d'études analytiques, Centre d'études nucléaires de
Fontenay-aux-Roses, France
Nuclear Material Control Center, Tokai-Mura, Japan
Japan Atomic Energy Research Institute, Tokai-Mura, Japan
New Brunswick Laboratory, Argonne, USA
Oak Ridge National Laboratory, Oak Ridge, USA
Osterreichisches Forschungszentrum Seibersdorf, Austria
Central Bureau for Nuclear Measurements, Geel, Belgium
Centre d'étude de l'énergie nucléaire, Mol, Belgium
Bhabha Atomic Research Centre, Bombay, India
Central Research Institute for Physics, Budapest, Hungary
Enea-Eurex, Saluggia, Italy
Enea-Itrec, Cre-Trisaia, Policoro, Italy

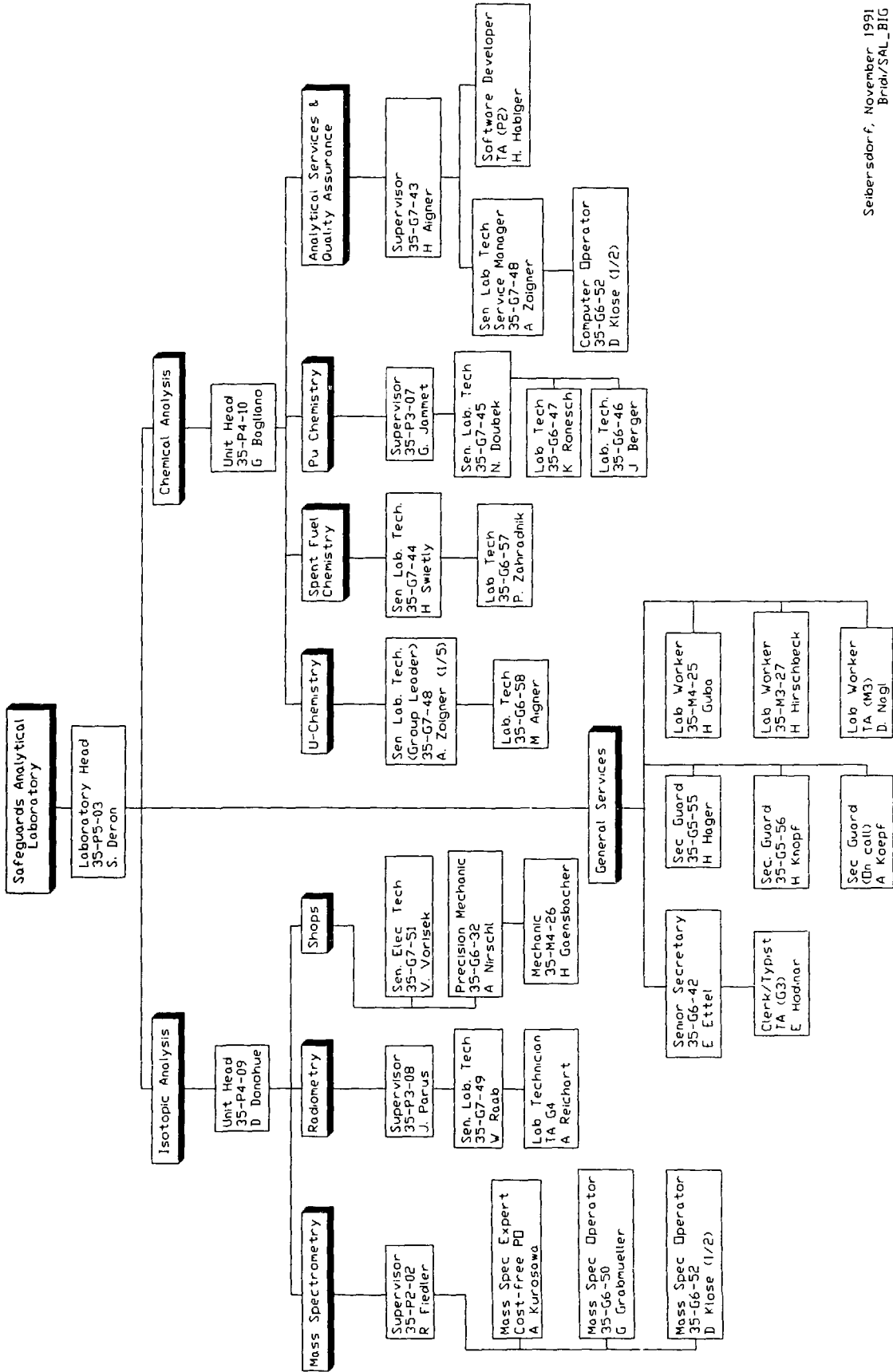


Figure 1a: General Organigramme of SAL

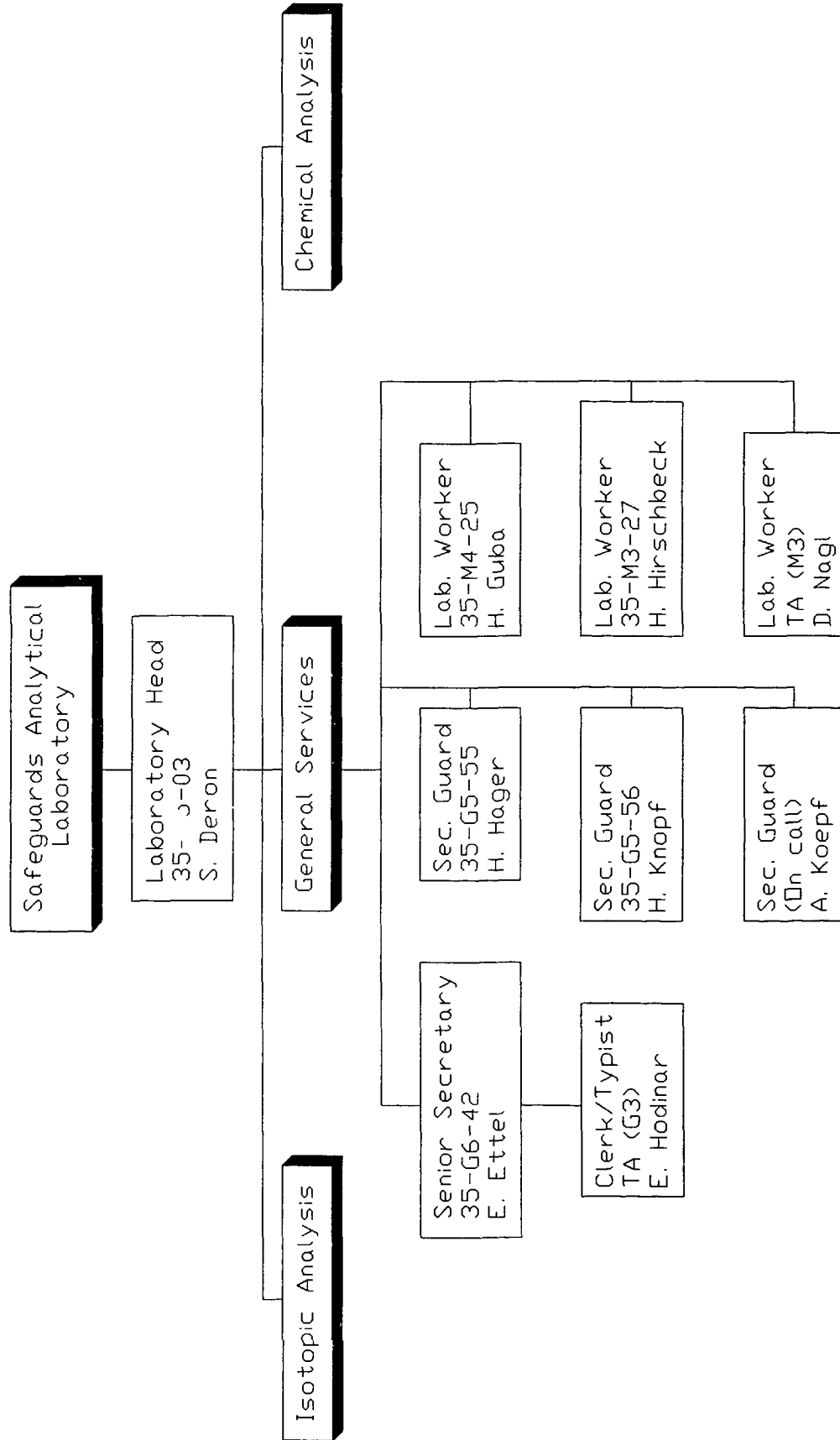
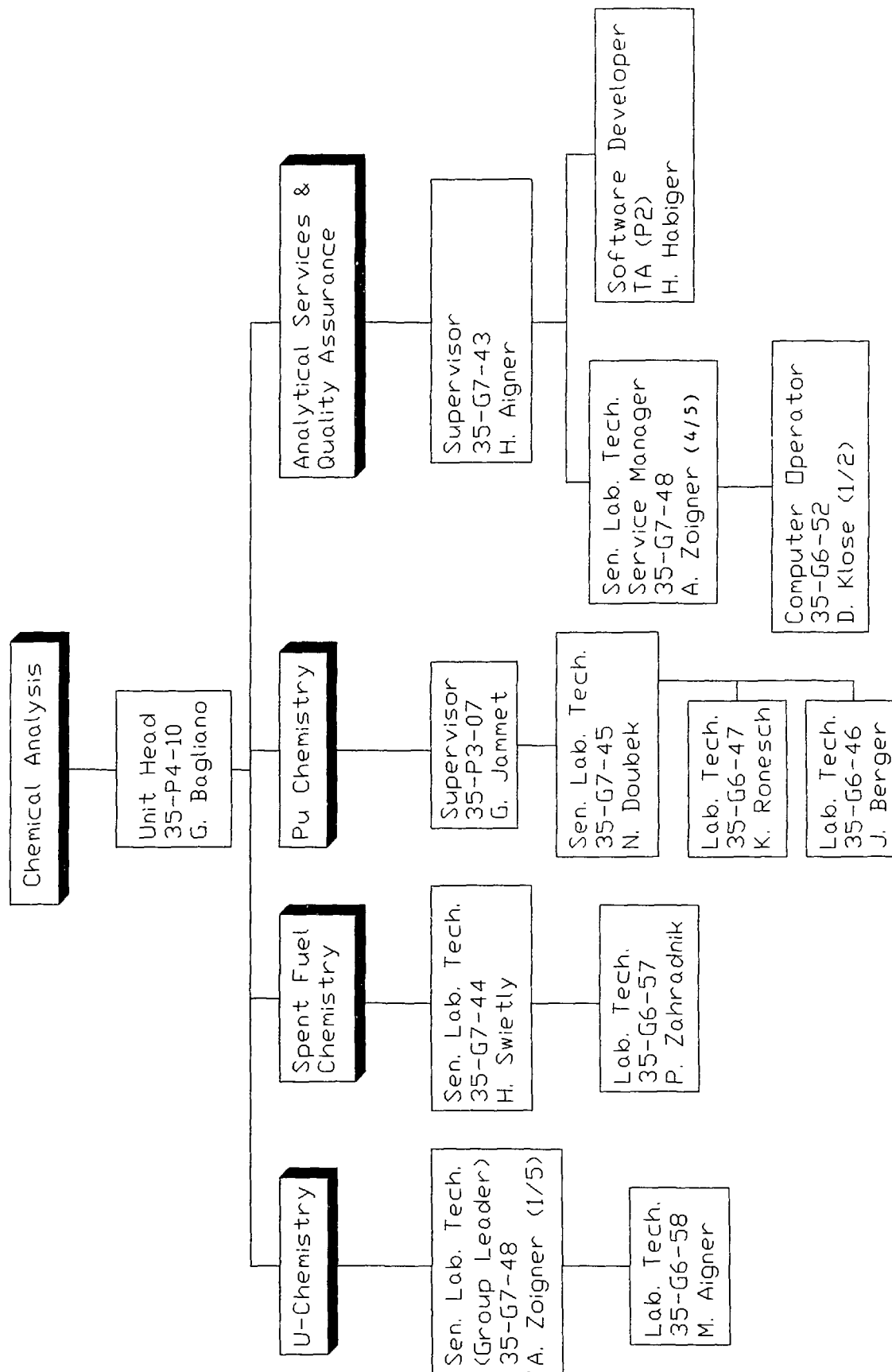


Figure 1b: Organigramme of SAL Chemical Analysis Unit



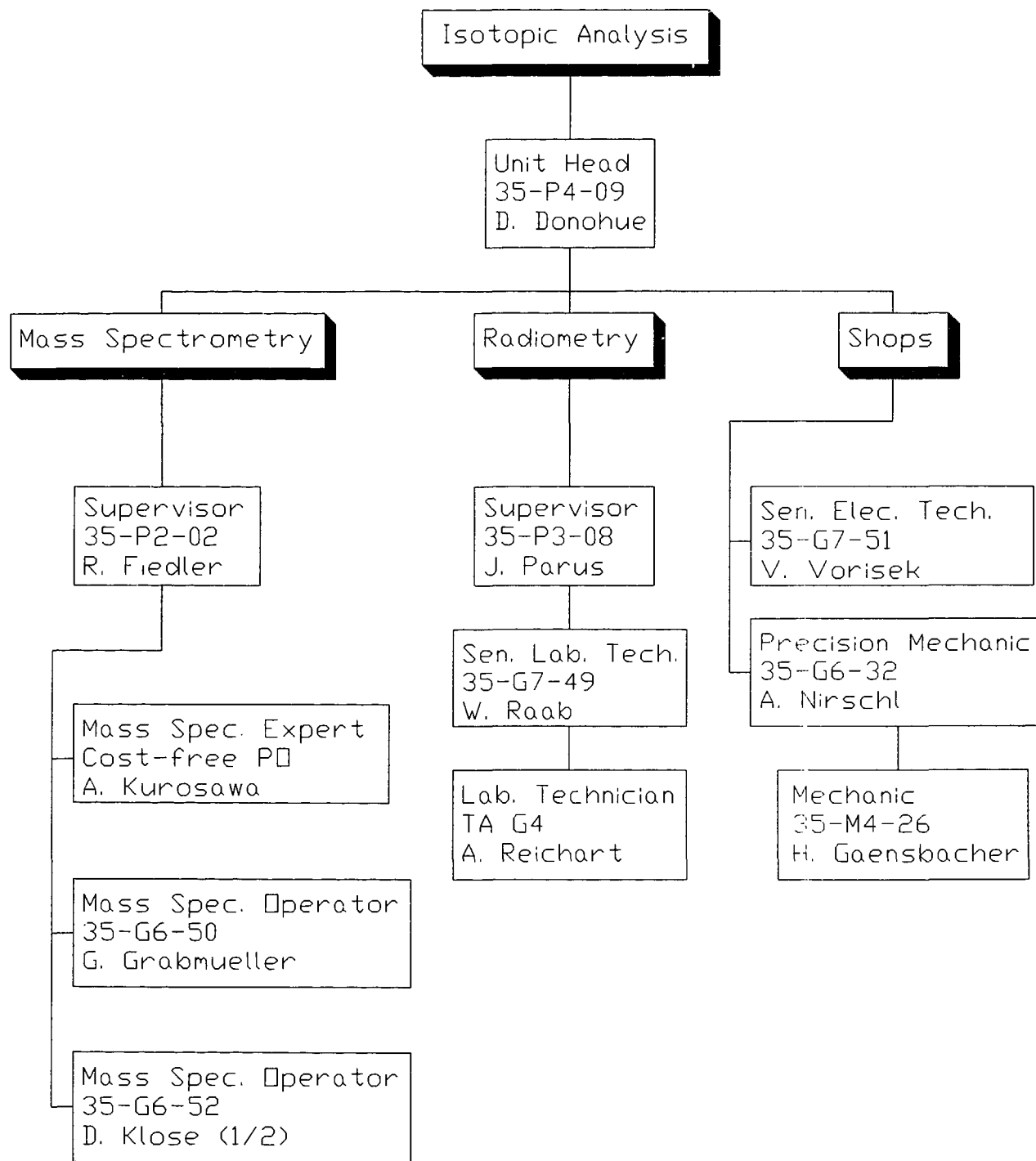


Figure 1c: Organigramme of SAL Isotopic Analysis Unit

2. Volume of the services rendered

2.1 Direct Verification measurements

While the total number of samples received annually had leveled around 1200 in the previous 2-3 years (Figure 2), there was an abrupt 25% increase in 1990 compared to 1989 (Table 2). The reasons were two fold. The number of spent fuel samples increased from 72 to 382 because a second plant reprocessing safeguarded fuel returned in operation in 1990. In the same time the number of plutonium samples increased from 339 to 559 because several plutonium fuel fabrication plants produced significantly more fuel. It is worth noting that a good fraction of the plutonium product samples were sent for quick but accurate isotopic analysis in support of on-site NDA neutron coincidence assay.

Table 2 Inspection Samples of nuclear fuel materials received and analyzed in 1989 and 1990.

Year	1989	1990
Samples forecasted	1357	1464
Samples received	1278	1589
Samples analyzed	1199(6)	1512(184)
Carry over	109(23)	186(54)

() : Samples analyzed or still to be analyzed by the NWAL. Heavy water samples not included

Consequently 9 times more spent fuel samples were analyzed in 1990. Out of the 384 spent fuel samples analyzed in 1990, 141 samples were analyzed by the NWAL and 193 samples by SAL. The number of plutonium samples analyzed in 1990, all at SAL (536 samples) was about 58% higher than in 1989 whereas only 642 Uranium samples were analyzed by the analytical services in 1990, that is to say 181 samples less than in 1989; out of these 642 samples, 43 were analyzed by the NWAL and 599 by SAL. In 1990 one laboratory of the Agency's network performed a complete analysis on 41 heavy water samples whereas SAL analyzed a few of those samples. The contribution of the Agency's Network to the analyses of the inspection samples in 1990 is presented in table 3.

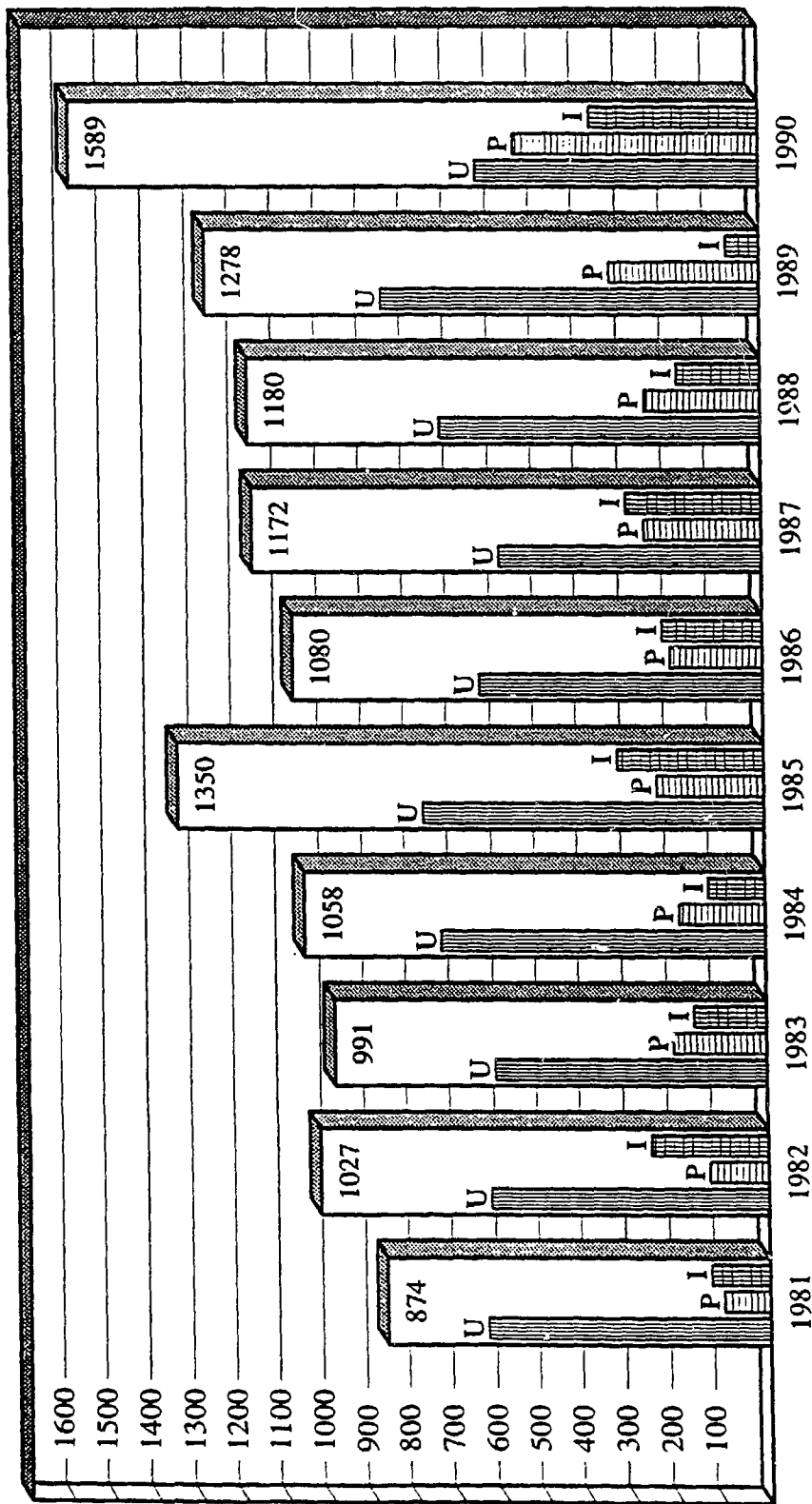


Fig. 2 - Samples received annually from 1981 to 1990

Table 3: Inspection samples analyzed by the NWAL in 1990

Laboratory	Number of samples analyzed		
	Unirradiated Uranium	Spent fuel	Heavy water
AERE Harwell (Didcot, UK)	13	18	
BAM (Berlin, FRG)	-	21	
CRIP (Budapest, Hungary)			41
NERF (Petten, Netherlands)	11	20	
NRI (Rez, Prague CSFR)	19	18	
OFZS (Seibersdorf, Austria)	-	24	
V.G.Khlopin Radium Inst. (Leningrad, USSR)	20		
ZRFR (Dresden, FRG)		20	
Total	43	141	41

A total of 3.890 results were reported to Safeguards in 1990, (Heavy water analysis results not counted). The type, the number of results reported and the contribution of SAL and the NWAL are shown in table 4.

Table 4: Number of results reported by the Safeguards analytical services on inspection samples in 1989 and 1990

Year	Measurement	Uranium	Plutonium	Americium	Total
1989	Isot.Comp.	940(64)	368(6)		
	Conc.	944(6)	312(6)	329	2893(82)
1990	Isot.Comp.	962(119)	856(141)	525	
	Conc.	941(119)	608(141)		3890(520)

(): Results originated at the NWAL and reported to SAL.

2.2 Non routine measurement performed by SAL

Table 5 lists the other analytical services provided by SAL in 1990.

In 1990 SAL characterized Uranium metal, products and scraps in the form of UO_x powder, yellow cake, U/Al oxide powder and strontium and uranyl nitrate solutions to be used as working standards for Non Destructive Analysis (NDA) in direct support of the Division of Safeguards Operations. (274 measurements were performed by SAL for this type of services).

SAL arranged also a test of the VOPAN (Verification of the OPERator ANalysis), an approach proposed by Dounreay (U.K.) as a timely and economical procedure for "on site" measurements (11) and demonstrated its vulnerability (12). SAL has performed analyses to test also on-site DA procedures for thermoquad mass spectrometer, X-ray fluorescence spectrometers, hybrid K-edge/X-Ray fluorescence instruments and to verify the procedure which uses a dried tracer (LSD-Spike) to spike directly the concentrated tank accountability solution and thus simplifies the sample treatment at the facility (13). A total of 1003 measurements were done by SAL for this type of services.

SAL has performed in addition 1393 measurements to test its own procedures or to improve them. These measurements concerned the setting up of a semiautomatic procedure of the modified MacDonald and Savage electrochemical titration of plutonium (14) and its adaptation to an automatic mode, the modification of the CEC-TOPO chemical separation (15) in view of its use by a robot accommodated in a glove box (16, 17), the checking of mass spectrometer techniques (18) and procedures aiming to improve the performances of its multidetector thermal ionisation mass spectrometers (19), and other developments using mass spectrometry as the measurement technique.

About 370 measurements had to be done at SAL to certify working reference materials [e.g. the preparation and the validation of 5 different batches of large size dried spike (20, 21, 22, 23) and quality control materials for DA (e.g. the preparation and the validation of control samples for the LSD-3 and the LSD-4 spike batches)].

In total compared to 1989, SAL did about 22% more non routine measurements in 1990 mainly for maintaining, improving, and testing new procedures for off-site and on-site DA (overall 2396 measurements performed in 1990 on these topics against the 1912 in 1989). These figures show the serious effort of SAL to start in time to face the challenge of the new trends of Safeguards, i.e. the implementation of on-site DA procedures and safeguarding large thruputs of the fissile materials at new bulk handling facilities requiring more precise and accurate off site analytical techniques (9).

Table 5: Non routine measurements performed by SAL in 1990
(Total number: 3038)

Purpose of Analyses	Sample Type	Nber of Measurements
<u>1. Calibration and Quality Control of on-site Non Destructive Analysis</u>		
Preparation and Verification of Working Ref. Materials for	UOx scraps	18
Calibration of an on-site XRF spectrometer	UNH	12
Characterisation of yellow cake	NH ₄ Diuranate	56
Characterisation of NDA Stds.	U/Al oxide powder	38
" "	U metal	72
Control of the calibration of an on-site XRF spectrometer	Sr(NO ₃) ₂ solution	25
Characterisation of working Ref Mat	UO ₂ powder	53
	<hr/> Subtotal	274
<u>2. Certification of Working Ref. Materials for off-site Destructive Analysis (D.A.)</u>		
Tank calibration	UNH dried mg size	12
Validation of 5 batches of large size dried spikes (LSD)	U, Pu synth.mix.	182
Preparation and validation of 2 batches of LSD control samples for LSD-3/LSD-4	"	54
Verification of two batches of small size dried tracer	CBNM-046/2	70
Validation of metallic spike	CBNM Pu, U metal	5
Verification of a plutonium tracer	Pu nitrate solut.	8
Verification of a control MOX sample	NBS960+SAL9925 solution	13
Preparation and validation of a MNH mg control sample	U, Pu synth.mix.	24
	<hr/> Subtotal	368

Table 5 (cont'd): Non routine measurements performed by SAL in 1990
(Total number: 3038)

Purpose of Analyses	Sample Type	Nber of Measurements
<u>3. Maintenance Improvements and Quality Control of off-site DA</u>		
Intercomparison test of IDMS performed at SAL and at OFZS	Pu, U synth mix. mixed with a four isotope tracer	8
Analysis of contamination on outside vials of spent fuel vials	Dried spent fuel	3
Adapt CEC-TOPO sep. to automate in glove box	Pu, U, synth. mix	178
Mass Spec Support of Chemistry development	Pu, U synth mix	92
Mass Spec system calibration	Isot.Std.Ref.Mat.	78
Mass Spec Instrument tests	Isot.Work.Ref.Mat.	110
Mass Spec tests procedures and developments	Various U and Pu products	242
Isotopic dilution alpha spec exercise	Dil. spent fuel	28
Total evaporation Mass spec test	U isot. Ref. mat.	4
Adapt the MacDonalld and Savage titration procedure to the automatic mode	Pu and Pu+U sol.	650
	<u>Subtotal</u>	<u>1393</u>
<u>4. Testing Procedures for on-site D.A.</u>		
In field test using che LSD-2	Dil.spent fuel	102
Mass Spec tests of procedures and development using a THQ	POX and MOX products	200
Prep and measurements of U beads for XRF techniques	UOx, ThOx fused with $\text{Li}_2\text{B}_4\text{O}_7$ +18% Li_2O_3 or with $(\text{NaPO}_3)_6$	300
Determ of U Th oxide powder by hybrid Kedge/K-XRF	U, Th oxides	50
VOPAN vulnerability test	U products	351
	<u>Subtotal</u>	<u>1003</u>
	<u>Total</u>	<u>3038</u>

2.3. Non routine measurements performed by the NWAL

The analytical thruput of the NWAL for non routine analysis in 1990 (869 measurements) was about 13% higher than in 1989 (771 measurements) in spite of the much larger contribution of the NWAL in 1990 compared to 1989 for the analysis of the inspection samples (see tables 3 and 4). This is the result of the coordination efforts of the steering group of the analytical services to cope with the challenge mentioned in the above last paragraph within the limitations of the prevailing financial restrictions.

Table 6 shows that 110 out of the 869 measurements were performed to characterize a Uranium metal used as NDA working standards. Another 300 measurements were carried out to validate two batches of LSD-spikes, to check the stability of a spent fuel control sample and to test a procedure for tank calibration. Testing an in-field application of the LSD-2 spike required 34 measurements and the adaptation of the MacDonald and Savage electrochemical titration to an automate mode (shared task with SAL) needed another 425 measurements.

3. Quality of Services

3.1. Delays

Table 7 shows an impressive decrease of the delays of the preparation of the samples at the facility before shipping and the time of shipping itself for the unirradiated uranium and plutonium samples (respectively 25% and 45% lower in 1990 compared to 1989). This is the result of the great effort of the responsible group of SGDIM to organize and streamline the shipment from the facility to SAL. The group needs for this to interact continuously with the inspectorate to track the parcels in their way to SAL and to request the inspectorate to reduce as reasonably as possible in agreement with the operator the time needed for the samples conditioning at the facility before their shipment to SAL.

The average time needed in 1990 for the preparation and shipment of spent fuel samples was typical of the delays observed in inspections at a facility which was not in operation in 1989.

An increase is noticeable in the time needed to perform the analyses of spent fuel and uranium samples. In the case of spent fuel samples, this reflects the fact that SAL and NWAL worked close to their full capacity to accommodate almost a 5 fold increase in the number of the samples of this type. The increase of the time of analysis of uranium samples on the other side is the result of a decision to accept an analysis delay of up to 30 days for low enriched uranium samples. This still allows to meet easily the goal verification time of one year (24). This decision was taken in order to allow the chemist to start setting up a new automatic titrator, without diverting man power from the plutonium and spent fuel chemistry groups. For plutonium samples the delays of the analyses were about the same in 1990 and 1989, in spite of the fact that there were 58% more samples of this type analyzed in 1990.

Globally it is therefore not surprising that the total verification time for spent fuel solutions returned to the value observed in 1988. For uranium samples the total time remained stable and well within the target. The decrease by 22% for plutonium samples is remarkable (Figure 3).

Table 6: Non Routine Measurements performed by NWAL in 1990
(Total Number 869)

Laboratory (Type of Service)	Purpose of Analyses	Sample Type	Nber of measurements
<u>1. Calibration and Quality Control of on site NDA</u>			
ECN (Le Petten)	Characterisation of NDA Stds	U metal	110
<u>2. Certification of Working Reference material for off-site D.A.</u>			
OFZS (Seibersdorf, Austria)	Validation of 2 batches LSD-spike	U, Pu synth	84
NMCC-SAL (Japan)	Validation of 2 batches LSD spike	"	72
Khlopin Radium Institute (Leningrad, USSR)	Stability test of a spent fuel control sample	SAL9904:dil spent fuel	28
ORNL (Tennessee, USA)	Tank calibration	$^{176}\text{Lu}/^{175}\text{Lu}$ solution	116
		subtotal	300
<u>3. Maintenance Improv. and Quality Control of off-site DA</u>			
NRI (Rez, CSFR)	Adaptation of the MacDonald and Savage procedure to the automatic mode	Pu and Pu+U solutions	425
<u>4. Testing Procedures for on-site D.A.</u>			
NMCC-SAL (Japan)	In field test of LSD-2 spike	Dil.spent fuel	34
		Total	869

Table 7: Time needed for Verification by Destructive Analysis in 1990 compared to 1989 (Median delays in days/sample)

Category of samples	Sample preparation + shipment delays		Analysis delays		Total verification time (a)		Timeliness factor (b)	
	1989	1990	1989	1990	1989	1990	1989	1990
Uranium	28	21	16	22	50	49	0.1	0.1
Plutonium	42	23	21	20	62	48	2.1	1.6
Spent Fuel	10	45	15	24	23	70	0.8	2.3

(a) Total verification time: Time elapsed from the starting day of the sample preparation at the facility to the day of the report of the analytical results to the Safeguards Liaison Officer.

(b) Timeliness factor: Ratio of the median mean total verification time to the goal detection time defined for each category of nuclear material (3)

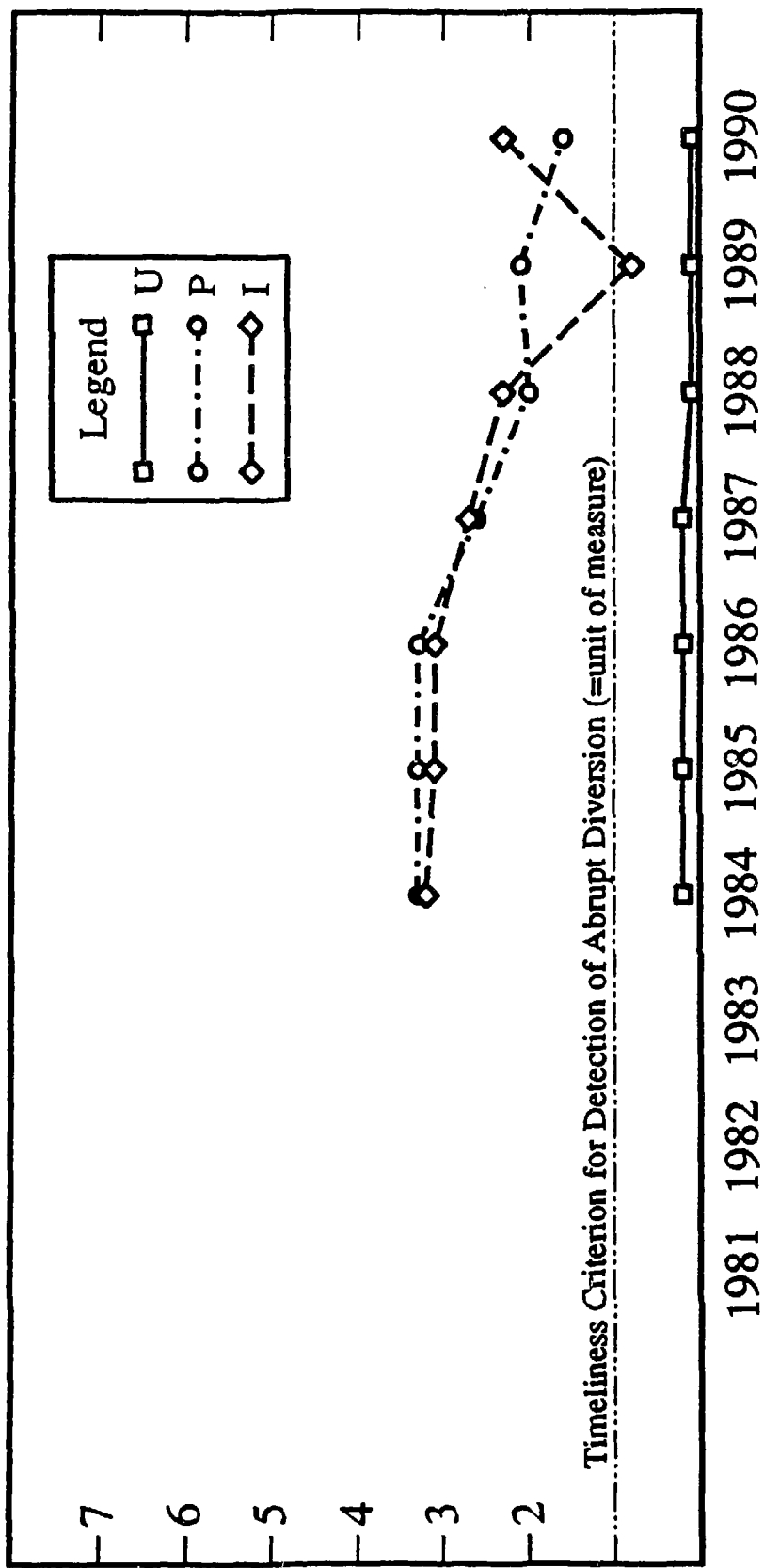


Fig. 3 - Total Verification Time for Destructive Analysis (based on MEDIAN values)

3.2 Quality Control of the Measurements

3.2.1. SAL's Internal Quality Control Programme

SAL's Internal Quality Control Programme (25) involves:

the calibration of the final analytical measurements and the control of the stability of this calibration using certified reference materials;

the control of the complete analytical process by analyzing well known or certified control materials along with the samples;

the control of the repeatability of duplicate analyses of the sample;

the comparison of results obtained by independent methods or different laboratories.

Control charts are issued weekly, displaying the random errors of the analyses of reference and quality control materials, their bias as well as the cumulated biases according to a modified Page test. The tables 8 give examples of the results of quality control measurements of various sources. The following observations have been made:

- (1) The results obtained with reference materials of different origins or chemical compositions are in good agreement and usually consistent with the certified accuracies.
- (2) The slight positive bias observed with CBNM-072/1 probably reflects incomplete control over mass fractionation.
- (3) The negative bias on the $^{242}\text{Pu}/^{239}\text{Pu}$ ratio of NBS 947 is within the certified accuracy, but is also observed by other NWAL's (26).
- (4) The results of alpha spectrometry measurements of the ^{238}Pu and ($^{239}\text{Pu} + ^{240}\text{Pu}$) activity ratios indicate that the certified value is probably much more accurate than stated in the certificate ($\pm 2\%$).
- (5) The "old" set of uranium isotopic standards of NBS is well suited for the calibration and quality control of ^{235}U abundance measurements by destructive gamma spectrometry.

Table 8a: Results of Quality Control of Radiometric Measurements in 1990
(Relative differences to goal values, in %)

Method	Measurement	Material	Mean	Standard Error	Random Error (M)	Systematic Error (K)
Gamma Spec Calibration	²³⁵ U wt%	NBS-010	0.015	0.025	0.111	-
		NBS-015	-0.013	0.016	(20)	(1)
		NBS-015	-0.013	0.016	0.073	-
					(20)	(1)
		NBS-020A	-0.075	0.025	0.080	-
					(10)	(1)
Gamma Spec QC*	²³⁵ U wt%	NBS-020	0.077	0.013	0.060	-
					(20)	(1)
		NBS-030	-0.020	0.016	0.073	-
					(20)	(1)
HRGS**	²⁴¹ Am/Pu	NBS-947	-0.818	0.219	1.067	0.321
					(263)	(3)
	²³⁸ Pu/ ²³⁹ Pu	"	0.347	0.148	0.927	0.210
					(263)	(3)
	²⁴⁰ Pu/ ²³⁹ Pu	"	0.794	0.341	1.032	0.516
Alpha Spec	²⁴¹ Pu/ (²³⁹ Pu+ ²⁴⁰ Pu)	NBS-947	0.080	0.053	0.369	0.098
					(192)	(5)

* QC: Quality Control

** HRGS: High Resolution Gamma Spec.

Table 8b: Results of Quality Controls of Mass Spectrometry Measurements in 1990
(Relative differences to goal values, in %)

Method	Measurement	Material	Mean	Standard Error	Random Error (N)	Systematic Error (K)
Mass Spec.	$^{240}\text{Pu}/^{239}\text{Pu}$	NBS-947	-0.043	0.007	0.032 (205)	0.042 (49)
	$^{242}\text{Pu}/^{239}\text{Pu}$	"	-0.343	0.023	0.103 (205)	0.141 (49)
	$^{242}\text{Pu}/^{239}\text{Pu}$	NBS-128	-0.205	0.009	0.000 (3)	-0.016 (5)
	$^{240}\text{Pu}/^{239}\text{Pu}$	UK/Pu3	0.021	0.009	0.034 (59)	0.038 (33)
	$^{242}\text{Pu}/^{239}\text{Pu}$	UK/Pu3	-0.032	0.022	0.105 (59)	0.086 (33)
	$^{240}\text{Pu}/^{239}\text{Pu}$	UK/Pu5	-0.023	0.008	0.040 (96)	0.038 (42)
	$^{242}\text{Pu}/^{239}\text{Pu}$	"	-0.008	0.018	0.113 (96)	0.073 (42)
	$^{244}\text{Pu}/^{239}\text{Pu}$	"	-0.051	0.033	0.177 (96)	0.154 (42)
	$^{235}\text{U}/^{238}\text{U}$	NBS-010	-0.037	0.015	0.098 (124)	0.076 (45)
		NBS-030A	-0.021	0.018	0.104 (64)	0.053 (33)
		NBS-100	-0.032	0.030	0.048 (8)	0.058 (6)
		NBS-200	-0.038	0.031	0.074 (20)	0.081 (11)
		NBS-500	-0.026	0.024	0.073 (40)	0.089 (24)
		NBS-930	0.045	0.025	0.445 (20)	0.094 (18)
	$^{235}\text{U}/^{238}\text{U}$	CBNM-072/1	0.096	0.058	0.090 (9)	0.092 (5)
	$^{233}\text{U}/^{238}\text{U}$	CBNM-072/1	0.115	0.084	0.092 (9)	0.147 (5)
	$^{235}\text{U}/^{238}\text{U}$	SSR-3568	-0.017	0.026	0.078 (13)	0.040 (10)
	$^{233}\text{U}/^{238}\text{U}$	SSR-3568	0.005	0.047	0.129 (13)	0.088 (10)
	$^{236}\text{U}/^{238}\text{U}$	SSR-3568	-0.038	0.019	0.058 (13)	0.028 (10)

Table 8c: Results of Quality Controls of Isotope Dilution Mass Spectrometry Measurements in 1990
(Relative differences to goal values, in %)

Method	Measurement	Material	Mean	Standard Error	Random Error (N)	Systematic Error (K)
U-Blank (GB)*	$^{233}\text{U}/^{238}\text{U}$	CBNM-040/1	-14.4	3.79	7.68 (38)	9.48 (15)
U-Blank (FC)**	$^{233}\text{U}/^{238}\text{U}$	CBNM-040/1	-8.5	2.66	1.02 (17)	7.03 (9)
Pu-Blank (GB)	$^{242}\text{Pu}/^{239}\text{Pu}$	CBNM-049	-4.6	0.69	4.24 (68)	1.92 (23)
Pu-Blank (FC)	$^{242}\text{Pu}/^{239}\text{Pu}$	CBNM-049	-0.022	0.536	2.13 (17)	0.410 (10)
Spent Fuel Chem.	Pu ($\mu\text{g/g}$)	samples	69.6	4.35	38.8 (186)	25.8 (81)
Pu Lab chem	Pu ($\mu\text{g/g}$)	"	75.2	5.80	25.0 (525)	60.7 (203)
IDMS (PuLab)***	LEU	NBS-960	0.187	0.041	0.044 (49)	0.251 (42)
	HEU	NBL-116	-0.307	0.071	0.245 (12)	- (4)
	LEU	SAL 9307	-0.113	0.026	0.099 (14)	- (4)
	Pu	NBL-126	-0.121	0.024	0.084 (13)	- (7)
		SAL9917	-0.035	0.199	0.133 (47)	0.349 (4)
		SAL9925	-0.171	0.024	0.143 (44)	0.052 (29)
		SAL9953	0.061	0.013	0.000 (5)	0.024 (4)
		SAL9304	-0.029	0.036	0.079 (33)	0.056 (4)
		SAL9947	-0.239	0.027	0.044 (6)	0.028 (2)
IDMS with QS87****	LEU	CL87	-0.056	0.035	0.036 (60)	0.146 (21)
IDMS (spent fuel Lab)	LEU	CL87	-0.053	0.065	0.358 (30)	- (4)
	Pu	CL87	0.165	0.138	0.176 (30)	0.244 (4)

* : G.B. Glove Box in the Pu Lab
 ** : F.C. Fume Cupboard in the Spent Fuel Lab.
 *** : IDMS Isotopic Dilution Mass Spectrometry
 **** : QS87: Quadruple Spike prepared in 1987

Table 8d: Results of Quality Controls of Titrations in 1990
(Relative differences to goal values, in %)

Method	Measurement	Material	Mean	Standard Error	Random Error (N)	Systematic Error (K)
DG* autom.	U-calibration	NBS-960	-0.085	0.016	0.044 (402)	0.125 (78)
	U-control	EC-110	-0.009	0.006	0.056 (140)	0.019 (24)
DG manual	U-calibration	NBS-960	-0.008	0.009	0.036 (14)	0.000 (5)
	U-control	EC-110	-0.066	0.016	0.019 (4)	0.032 (4)
Ignit.Grav.	Th	JM	-0.120	0.002	0.045 (7)	0.026 (3)
DG (40mg)	U-calibration	NBS960	-0.039	0.011	0.052 (72)	0.037 (18)
	U-control	EC-110	-0.050	0.022	0.051 (38)	0.097 (18)
MDS**	Pu-calibration	NBS-949	-0.225	0.040	0.061 (36)	0.138 (13)
		EC-201	-0.255	0.043	0.086 (4)	- (1)
		MP2	-0.126	0.097	0.062 (16)	0.188 (4)
		UK/Pu1	-0.151	0.040	0.067 (34)	0.118 (10)
MDS manual	Pu-control	NBL122	0.009	0.030	0.064 (54)	0.068 (13)
		NBL126	0.023	0.030	0.070 (14)	0.102 (14)
		NBL-126	0.018	0.018	0.056 (10)	- (3)
MDS autom.	Pu-control	NBL-122	0.121	0.012	0.027 (5)	- (1)

* : DG: NBL modified Davies and Gray potentiometric titration

** : MDS: Mac Donald and Savage potentiometric titration scaled down to 4mg of Pu.

Table 9: IDMS results obtained by the NWAL in 1990 in control samples spiked with a LSD* tracer (Differences to certified values in %)

LAB	STATISTICS	Pu	U
A	Mean	-0.01	-0.11
	Std. Dev	0.10	0.10
	(n)	(21)	(8)
B	Mean	+0.07	-0.08
	Std. Dev	0.19	0.02
	(n)	(2)	(2)
C	Mean	+0.24	-0.04
	Std. Dev	0.09	0.09
	(n)	(2)	(2)
D	Mean	+0.07	-0.09
	Std. Dev	0.08	0.13
	(n)	(3)	(4)
E	Mean	+0.05	+0.13
	Std. Dev	0.05	0.12
	(n)	(2)	(2)
F	Mean	-0.06	-0.07
	Std. Dev	-	0.11
	(n)	(1)	(2)
G	Mean	+0.06	-0.01
	Std. Dev	0.16	0.01
	(n)	(4)	(2)

* LSD: Large Size Dried

3.2.2. A Quality Programme for the Spent Fuel Samples Analysed by the NWAL

The programme proposed in 1985 (27) was reviewed in a Consultants' group meeting in Dec. 1990 (28). The IDMS results obtained by the NWAL in control samples spiked with a LSD tracer are shown in table 9 and are discussed in (29). The coefficients of variations and relative biases are with one exception smaller or equal to 0.1%.

3.2.3. Participation in Independent Analytical Quality Control Programmes

Well characterized materials needed to estimate the magnitude of uncorrected calibration errors combined with the treatment errors have been available for SAL since the end of 1985. The results obtained in 1990 with Uranyl and plutonium nitrate solutions are shown in Table 10. The relative biases are not statistically different from zero, compared with their standard errors which are equal to 0.078%.

Table 10: Results of SAL analyses of plutonium nitrate solutions distributed in 1990 within the EQRAIN * programme

Sample/ Period	Method	Result (mg/g)	% bias
1	Automatic	4.0460	0.127
	Manual	4.0486	0.092
2	Automatic	4.9142	-0.109
	Manual	4.9964	-0.065

* EQRAIN: "Evaluation de la Qualité des Résultats d'Analyses dans l'Industrie Nucléaire."

4. Maintenance and Development of Analytical Procedures

We describe here the principal achievements in the three areas of analytical development pursued in 1990.

4.1. Off-site Destructive Analytical Procedures

4.1.1. Implementation of the Large Size Dried Spike Method

The Large Size Dried (LSD) Spikes are in use since March 1990 for the Isotope Dilution Analysis (IDA) of spent fuel solution samples taken from the input accountability tank of a reprocessing plant. The method involve the following steps (13): a sample of about 1 ml of the undiluted spent fuel solution is weighed into a penicillin vial containing a calibrated LSD spike; the spike consists of a mixture of dried nitrates carrying about 2 mg of 97% enriched ^{239}Pu and 50 mg of 19 % enriched ^{235}U ;

the vial is heated after addition of 8M nitric acid, to dissolve the spike quantitatively; the solution is stirred, 50 μ l aliquots are taken, dried, bagged out and packed for shipment to the inspectorate laboratories, where the contents of uranium and plutonium are determined by mass spectrometry. Duplicate spiked samples and one unspiked samples are prepared, shipped and analyzed simultaneously. The operator takes parrallel aliquots and uses them for its accountability analyses.

The spike is prepared from primary reference materials such as NBL 126 (Pu), NBL-112A (natural U) and NBL-116 (HEU), alternatively by IAEA-SAL and the State inspectorate laboratory. The certificate of the spike is based on the "make-up" values, validated by parrallel analyses at the inspectorate laboratories (20, 22, 23).

The LSD spikes replace the "small size" dried spikes which were used earlier and contained about 1 mg of ^{233}U and 5 μ g of ^{242}Pu tracer isotopes; the previous procedure required a 150 fold dilution of the spent fuel solution sample before spiking could be done. The main advantage of the new method is to permit spiking of undiluted samples. The dilution and the aliquoting need no longer to be done very accurately, the aliquots are much smaller and dry much faster, so that the complete preparation of the samples at the plant takes no more than 2 hours and requires much less of inspectors' and operators' time.

The operator went actually as far as installing a robot in a hot cell to perform the whole preparation fully automatically. Unfortunately the robot failed too often and the use of tongs had to be resumed to handle the sample vials. Several cases of cross contaminations occurred in the beginning; their origins were identified and have now been eliminated for the most part. Table 11 illustrates the performances achieved by the two methods, when cases of cross contaminations are eliminated. The LSD method has smaller random errors. The use of LSD spikes with tracer isotopes of closer masses largely compensate the disadvantage of their lower isotopic abundances. The very small fluctuations of the systematic errors is the expected benefit of the operator using inspectors' spikes. It reflects also the fact that uncorrected mass fractionations are smaller when using ^{235}U , ^{239}Pu or ^{240}Pu tracer isotope than when ^{233}U , ^{242}Pu or ^{244}Pu are used.

Table 11: IDMS of spent fuel solutions using small and Large Size Dried Spikes; Relative Standard Deviations of random and short term systematic errors in operator - inspector differences

Std. Deviation of Rel. Differences	Spike Size	
	Small	"Large"
Random Error	0.73	0.44
Syst. Error	0.66	0.04
Nber of Batches	247	139

The new procedure has however at least four features which may limit its performance and will continue to receive the attention of SAL and of the IAEA inspectorate. The shelf time of the spikes depends upon the ability to dry the spike salt at the bottom of the penicillin vials in the form of a film which remains adherent to the glass even during transport, and for at least 8 - 10 months. The current LSD procedure involves also no redox cycle of the sample aliquots before they are received and analyzed at the laboratories. Thirdly, errors in the assigned composition of the spike no longer appear in the differences between operator's and inspector's data and cannot be detected without additional and independent measurements. Finally the 97% enriched ^{239}Pu tracer is not suitable for the IDA of low burn-up fuels, in which the ^{239}Pu abundance exceeds about 80%.

The route we pursue to resolve these matters in collaboration with CBNM and other Network Laboratories is:

- to apply a comprehensive control of the quality of the certification and of the shelf-time of the spikes,
- to accumulate experience on the shelf time of spikes dried via alternative methods,
- to encourage the development of commercial sources of certified LSD spikes, in the form of dried nitrates or metal alloys, based preferably on mixtures of high enriched ^{240}Pu and ^{236}U isotopes.

4.1.2. Titration of 4 mg Pu with the McDonald & Savage Method

The method of Mc Donald and Savage had been selected to replace the AgO method because it is not vulnerable to interferences of Cr, Mn and many other species (30). The original procedure designed for titrating 30-40 mg Pu aliquots had been scaled down with the assistance of experts of Dounreay (31), Harwell (32) and Rez (33). The scaled down procedure uses potentiometry rather than amperometry to follow the titration of 4 mg Pu aliquots. It had been demonstrated to be as selective as the original method (34). In 1989-1990 all steps of the procedure, except the sample changing, were automated by combining two Radiometer Video titrators controlling each an ABU 3 multiple buret stand. This semi automated procedure has a repeatability of 0.05 to 0.10% and is also as selective as the original one (35).

An automatic turn-table was designed to automate fully the procedure and was installed in a glove box. The component tests were completed in September 1990 and tests with plutonium started in October 1990.

4.1.3. Separation of Uranium and Plutonium by column Extraction Chromatography

A. Delle Site et al. (36) introduced at SAL in 1985 a very efficient and versatile chromatographic separation of uranium and plutonium. In the original procedure hexavalent uranium and tetravalent plutonium were absorbed from a 3 N nitric acid solution on a stationary phase consisting of a porous polyethylene (microthene) coated with Trioctylphosphine oxide (TOPO). Americium and fission products are not retained. Plutonium is eluted with a solution of HCl (1N) and HI (0.1 N) which reduces plutonium to the trivalent state. Uranium itself is eluted next with a solution of ammonium carbonate. The microthene support has now been replaced by a silica support, Fractosil, which is easier to load on the column because its density is greater than one. The method constitutes the basic procedure at SAL for the preparation of plutonium and spent fuel samples for isotopic analysis or isotope dilution assay by mass and alpha spectrometry.

It was demonstrated in 1990 that plutonium can also be eluted with a mixture of 2 N nitric acid, 0.1 N iodhydric acid and 0.1 N sulfurous acid (37). The advantage of this reagent over the HCl/HI mixture is to be free of hydrochloric acid. Its use should therefore reduce the rate of corrosion of metal equipment in glove boxes. The concentration of the nitric acid must be kept between 1.5 and 2.5 N. At lower nitric acid concentrations uranium starts to elute with the plutonium; at higher concentrations the iodhydric acid oxidizes quickly to iodine despite the presence of sulfurous acid, plutonium is only partially reduced and cannot be eluted quantitatively.

The HNO₃/HI/SO₂ reagent will be used instead of the HCl/HI mixture in particular in the robot installed for the automatic preparation of spent fuel samples.

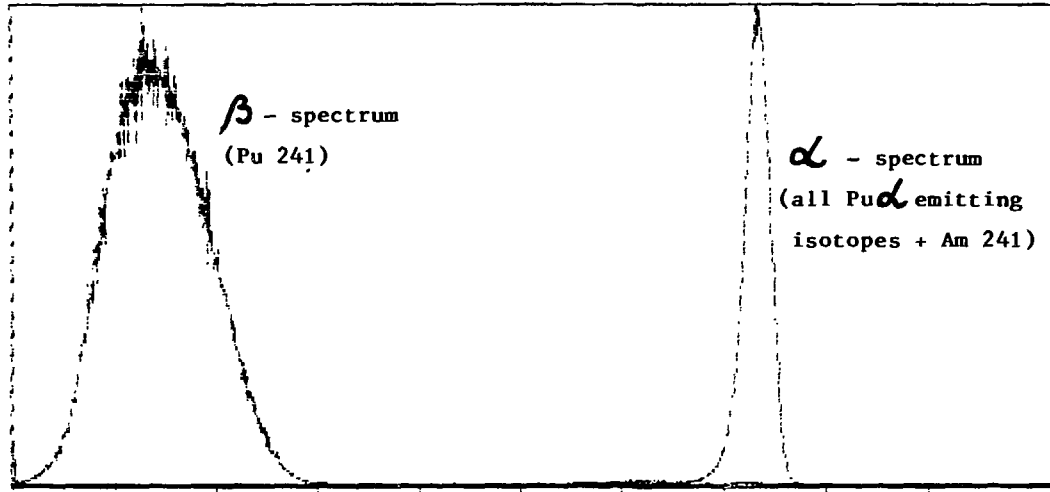
4.1.4. Alpha and Beta Liquid Scintillation

The radiometry group operates an automatic LKB liquid scintillation instrument. It is normally used to determine low concentrations of alpha and beta emitters. These measurements are calibrated against standard solutions of the analytes. The tuning of the instrument need normally little effort for such measurements.

In 1990, the instrument had to be carefully adjusted (38) to perform an absolute calibration of ²³⁸Pu and ²³⁹Pu spike solutions used for Isotope Dilution Alpha Spectrometry (IDAS). The pulse width filter had in particular to be optimized to segregate quantitatively the pulses resulting from the beta radiations emitted by ²⁴¹Pu isotope and the alpha radiations emitted by the other plutonium isotopes (Figure 4). It was found also that the counting efficiency of standard solutions of plutonium prepared from NBL 126 is only 99.85% when using the scintillation cocktail Hi Safe II (Pharmacia) in the way recommended by the manufacturer. Doping the cocktail with 4% of TOPO reduces the tendency of plutonium to plate on the walls of the scintillation vial and restores 100% counting efficiency. Finally counting activities exceeding 2500 cps identified an underestimate of the deadtime correction in the LKB software, which was rectified.

The specific activities measured at SAL after these tunings agree within 0.3% with the results obtained by two specialized laboratories (39) (Table 12).

[A] 971.279 CPM/ch 4.73 min \AM\AMTEST38\S0040101.001 SP#11
[B] 3301.808 CPM/ch 4.73 min \AM\AMTEST38\S0040101.001 SP#12



1 100 200 300 400 500 600 700 800 900 1000
INTEGR(1-1024) [A] 97767.930 CPM [B]106572.469 CPM
BUNCH= 1 * 3S * 431.317 (0.4 %) 450.320 (0.4 %)

Fig. 4: α and β spectra from liquid scintillation counter of Pu (NBL 126)

Table 12 Alpha Specific Activities of ^{238}Pu and ^{239}Pu spikes (in KBq/g)

Laboratory	Spike	
	^{238}Pu	^{239}Pu
SAL	156.55±0.04	201.19±0.04
1	156.4± 0.5	201.8± 0.3
2	156.8± 0.30	201.17±0.38
Overall Mean	156.58±0.20	201.39±0.36

4.1.5. Isotope Dilution Alpha Spectrometry of Plutonium

The two spikes mentioned in the previous section had been prepared by the Khlopin Radium Institute (KRI) in Leningrad for an interlaboratory test of the determination of plutonium in spent fuel solutions using IDAS. Besides SAL and KRI, the participants were AEA in Harwell, ECN in Petten and BARC in Trombay. They were to analyze aliquots of duplicate samples of a diluted spent fuel solution prepared and spiked by KRI. The results are presently being evaluated at KRI.

In this test SAL applied its standard method which involves a chemical equilibration based on a Fe(II)/NO_2^- redox cycle, a CEC separation on a TOPO/Fractosil support (36, 37), before the preparation of the alpha sources. These are prepared by depositing a 10 μl drop of solution containing about 0.2 μg of plutonium in a glazed porcelain cuvette, adding 10 μl of tetraethyleneglycol which serves as a spreading agent, and drying in a muffle furnace programmed to increase progressively the temperature from 25°C to 850°C. The source, which has an active diameter of 10 mm, is placed in a vacuum chamber at a pressure of 0.5 Pa and 15 mm away from an ion impacted surface barrier detector of 100 mm^2 area. The detector has an intrinsic resolution of 12 keV. The quality of the sources is sufficient to resolve the 5.45 MeV and 5.46 MeV peaks of ^{238}Pu , with a practical resolution of about 13 keV (Figure 5). Even with such a resolution, the method used to take the tailing of the peaks into account and the setting of the multichannel analyzer have still a measurable influence on the accuracy of the results.

SAL applied two methods of tail correction (40): in one method the tail is assumed to decrease exponentially with decreasing energies; in the other on the decrease is assumed to follow a geometric progression (41). IDAS agrees better with Isotope Dilution Mass Spectrometry (IDMS) when the geometric progression method is used (Table 13). The exponential tail modes is in better agreement with IDMS when a larger number of channels are used to define the tail decay constant. The other observation to be made on the results of SAL (Table 13) is that IDAS and IDMS are in best agreement when the $^{238}\text{Pu}/(^{239}\text{Pu} + ^{240}\text{Pu})$ alpha activity ratios do not exceed 5 in the spiked and unspiked samples.

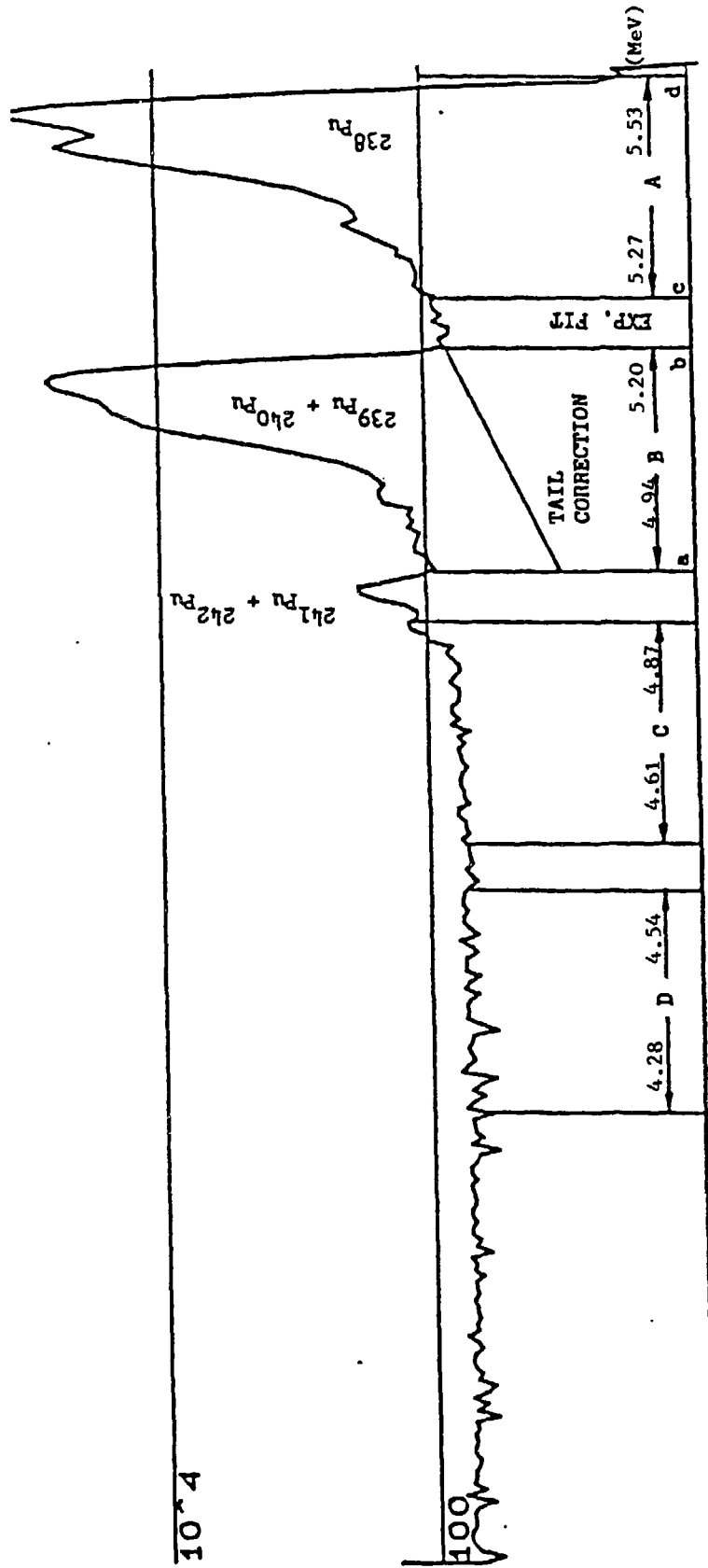


Fig. 5 Exponential decrease and geometric progression methods of tailing correction.

Table 13 Comparison of Results of Plutonium Assay by IDAS and IDMS

Method	Spike	Tail Correction (μ /g)	Pu Concentration	
			(a)	(b)
IDAS	^{239}Pu	Geometric Progression	7.479	7.454
		Exponential Decrease	7.478	7.450
	^{238}Pu	Geometric Progression	7.505	7.547
		Exponential Decrease	7.507	7.508
IDMS	NBL 126		7.451	
	QS 87		7.439	

(a) Energy Scale 4.20 keV/chan (1024 chan./spectrum)

(b) Energy Scale 2.10 keV/channel (2048 chan./spectrum)

Consequently we would recommend to use a ^{238}Pu spike only when the ^{238}Pu isotope abundance does not exceed 0.1% in the unspiked sample. For all other materials a ^{239}Pu spike containing less than 0.01% of ^{238}Pu is preferable.

4.1.6. High Resolution Gamma Spectrometry (HRGS)

The MGA2 algorithm was installed at SAL by R. Gunnink and W. Ruhter (41) in 1989. It is used to screen all plutonium samples submitted to SAL by HRGS for plutonium isotopic composition, ^{235}U , ^{239}Np and ^{241}Am abundances. The results of plutonium isotopic analysis obtained with 3 different planar detectors were compared to the results of destructive assays by mass and alpha spectrometry (42).

The comparison was done for a population of 498 samples divided into 4 material groups: 1) plutonium oxide (POX) - 90 samples, 2) plutonium - uranium nitrate hydrated (PNH), 3) mixed plutonium - uranium nitrate hydrated (MNH) - 151 samples, 4) mixed plutonium uranium oxide (MOX) - 143 samples. The following isotopic ratios measured by alpha ($^{238}\text{Pu}/^{239}\text{Pu}$) mass and gamma-ray spectrometry were compared: (238/239), (240/239) and (241/239). The results are presented in Table 14. The t-test was applied to investigate whether differences between the mass spectrometry assumed as a reference method and the gamma spectrometry results are significant or not. A linear regression function was calculated with the mass spectrometry values as an independent variable and the gamma spectrometry results as a dependent one. The deviations of the intercept from 0 and the slope from 1 were tested using two sided t-test at 0.05 significance level.

As can be seen from the Table 14 there are significant differences between MS : GS results at the assumed significance level for about two thirds of considered parameters. Besides some systematic errors were detected, particularly in 240/239 ratios. Further studies are undertaken by R. Gunnink in the framework of US support program to improve the quality of GS results.

Table 14 Comparison of the isotopic ratios using regression model $Y(\text{Calc.}) = A + B * X(\text{Mass Sp.})$ and calculated t-value for mean difference D between Mass Sp. values and values calculated using Gamma Sp.

I(238/239)

Mat. Type	t-test (D=0)	A	A-s.d.	t-test (A=0)	B	B-s.d.	t-test (B=1)	R-sq.
POX	0.00*	-0.00004	0.00003	-1.25*	1.0034	0.0019	1.79*	0.9996
PNH	0.63*	-0.0004	0.0001	-4.48	1.0226	0.0050	4.52	0.9979
MNH	9.72	-0.0006	0.0001	-6.40	1.0270	0.0058	4.65	0.9952
MOX	2.99	-0.0003	0.0001	-2.86	1.0121	0.0059	2.05	0.9951

I(240/239)

Mat. Type	t-test (D=0)	A	A-s.d.	t-test (A=0)	B	B-s.d.	t-test (B=1)	R-sq.
POX	2.75	0.0118	0.0053	2.22	0.9635	0.0140	2.61	0.9768
PNH	4.62	-0.0182	0.0046	-3.96	1.0404	0.0118	3.42	0.9887
MNH	8.61	-0.0063	0.0043	-1.47*	1.0074	0.0112	0.66*	0.9818
MOX	7.54	0.0104	0.0050	2.06	0.9591	0.0135	-3.02	0.9728

I(241/239)

Mat. Type	t-test (D=0)	A	A-s.d.	t-test (A=0)	B	B-s.d.	t-test (B=1)	R-sq.
POX	0.93*	0.0004	0.0004	0.97*	0.9977	0.0034	-0.67*	0.9987
PNH	4.27	-0.0033	0.0009	3.57	1.0177	0.0064	2.76	0.9965
MNH	13.08	-0.0038	0.0008	-4.71	1.0187	0.0064	2.92	0.9941
MOX	5.27	-0.0012	0.0008	-1.41*	1.0019	0.0071	0.26*	0.9929

* - H0 hypotheses are accepted at 0.05 level of significance (two-sided test)
 H0 : D=0 H0 : A=0 H0 : B=1

+ - the best results

A- S.d. = Standard Deviation of A values

B- S.d. = Standard Deviation of B values

4.2. On-Site Analytical Measurements

4.2.1. Anionic Exchange Separation for Thermoquad Mass Spectrometry

Independent isotopic analyses of plutonium were performed at a MOX fuel fabrication plant using a compact thermal ionization quadrupole mass spectrometer and total evaporation. The procedure requires an efficient chemical separation of plutonium from uranium so that the $^{238}\text{Pu}/^{239}\text{Pu}$ isotope ratio can be measured with an accuracy of 5% or better in spite of the potential isobaric interference of ^{238}U . The anionic exchange procedure in use by the plant laboratories was selected for this purpose and validated initially for the analysis of mixed oxides with U/Pu ratios up to 3/1 (43). The separation method has been extended now to accommodate samples with U/Pu ratios up to 20(44). It uses disposable micropolyethylene columns of 6 mm diameter filled with a Bio Rad AG 1-X8 resin of 100-200 mesh in nitrate form. Sample aliquots containing about 50 μg of plutonium are dissolved in 0.5 ml of 4N nitric acid, reduced with divalent iron and transferred on the columns which retains the plutonium in tetravalent state. Am and U are washed with 33 ml of 2N nitric acid. Pu is then eluted with 3 ml of a solution containing 0.2N nitric acid and 0.01N hydrofluoric acid (Figure 6). The results of isotopic analyses are expressed in weight percent effective ^{240}Pu according to the following equation:

$$\text{Effective } ^{240}\text{Pu} = 2.52 A(238) + A(240) + 1.68 A(242)$$

where A(i) are the measured isotopic abundances in weight per cent (45). Table 15 shows the results of measurements of a sample with a U/Pu ratio of 20.

Ion-Exchange Sep. with HNO₃ 2M

Vol. Adjustment: none

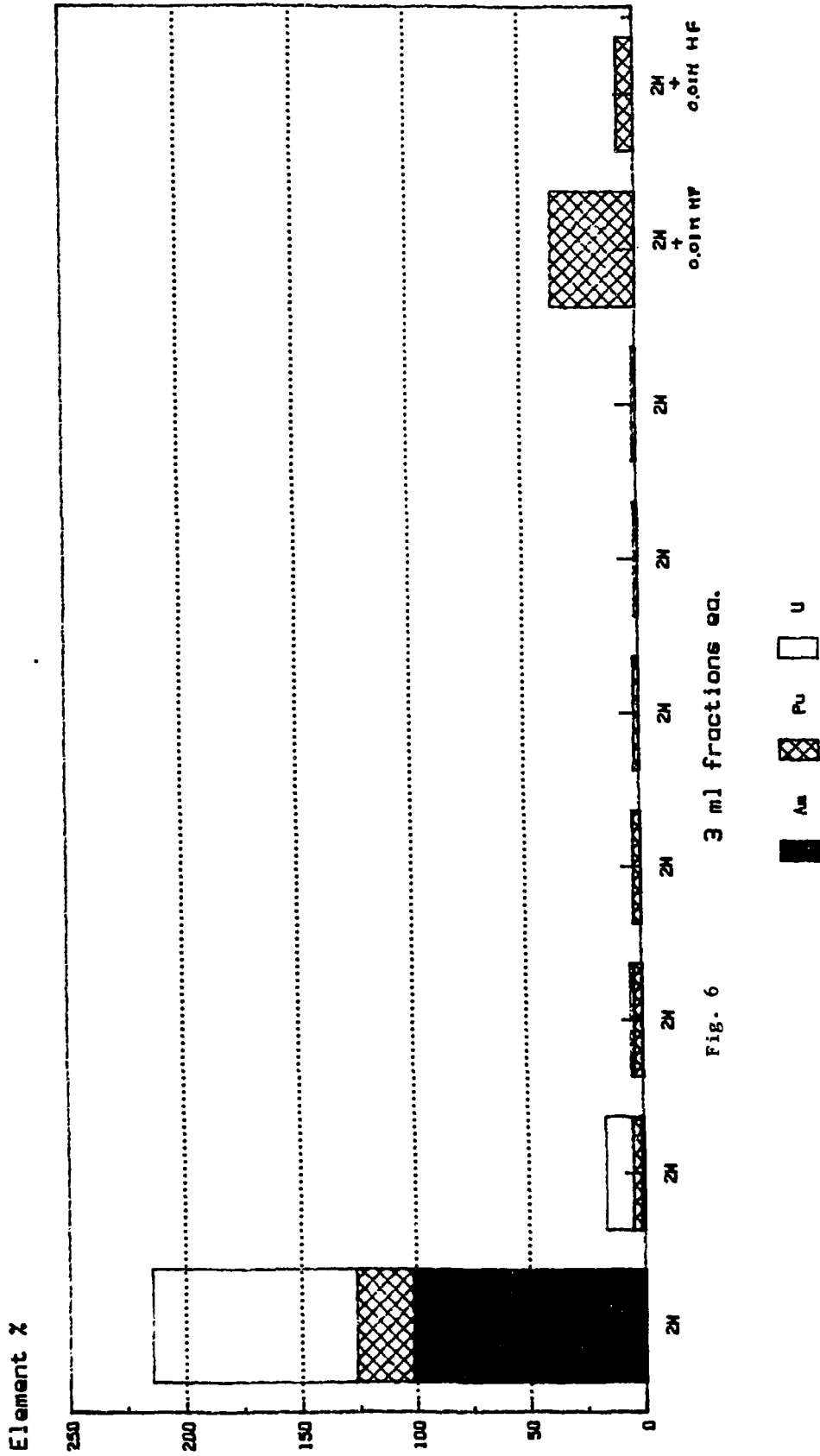


Fig. 6 3 ml fractions ea.

Table 15 Mass Spectrometric Determination of Effective ^{240}Pu abundances

Separation	Mean Difference (a) (in %) (b) (in %)	Std. Dev. of Relative Differences
1	0.22	0.11
2	0.11	0.02
3	0.06	0.01
4	0.05	0.01
5	0.10	0.01
Mean	0.10	0.05(c)
Std. Dev.	0.07	

(a) Relative Difference between results obtained after anion exchange (44) and column extraction chromatographic separations (36)

(b) Standard deviation of repeatability of replicate filament measurements

(c) Mean square

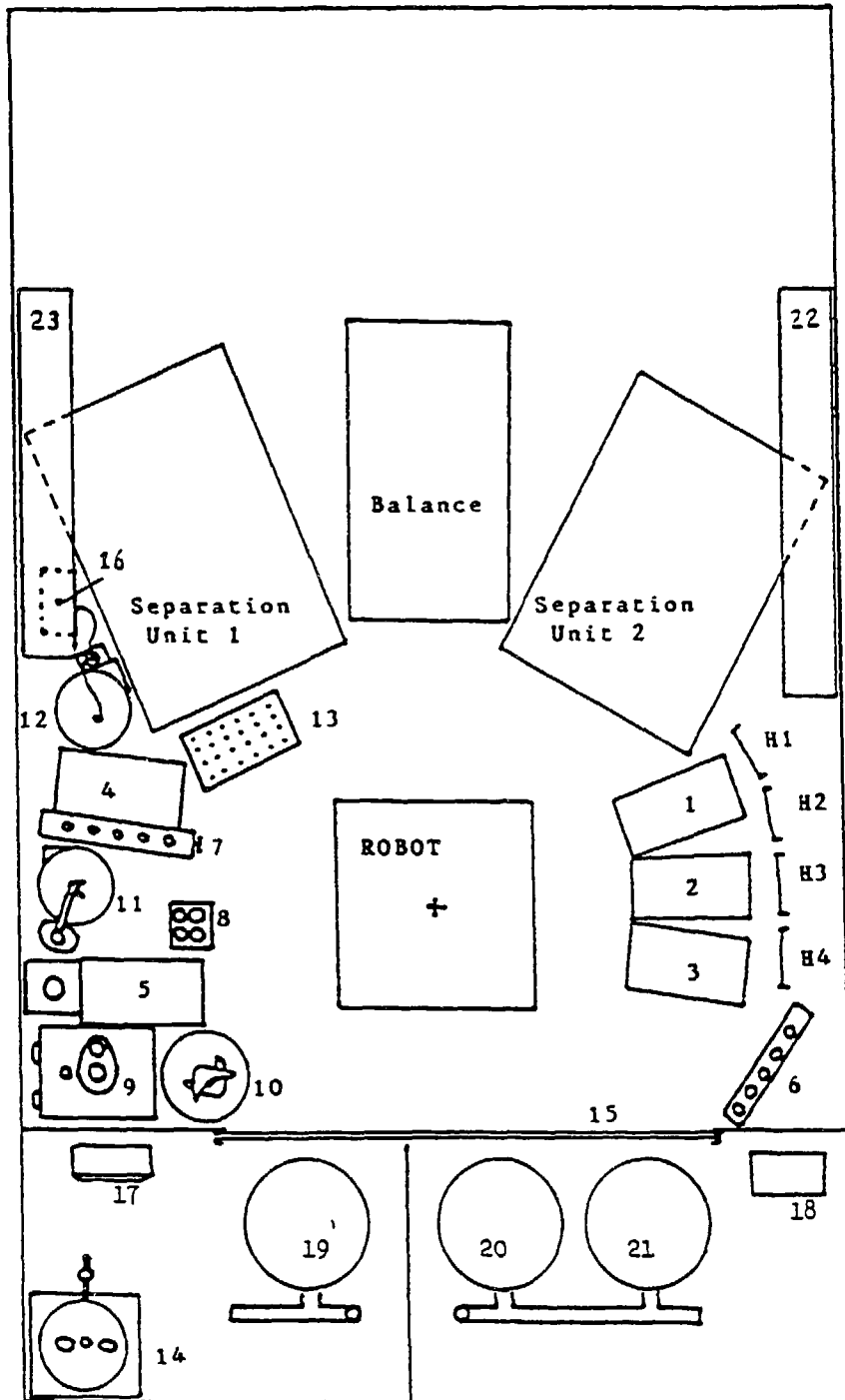
4.2.2. Chemical Robot for Spent Fuel IDMS

A robot was installed in SAL in 1989 with the assistance of the Transuranium Element Institute (Karlsruhe) (TUI) in the frame of the Cooperation of the IAEA and the European Economic Communities (EEC) for the Development of International Safeguards. It is designed to perform automatically the chemical preparation of spent fuel samples before their isotopic or isotope dilution analysis by mass and/or alpha spectrometry. The basic component of the instrument was designed by TUI around a Zymark robot arm (17).

SAL added in 1990 a column chromatographic unit to complete the installation. This unit will allow to perform up to 16 chemical separations simultaneously. Each column is equipped with an optical sensor which is placed just below its tip and monitors the growth of the drops of eluant. If the drop stops before the prescribed volume of eluant has flowed through the column, the top of the column is automatically covered with a pressurizing cap, a small aquarium pump increases briefly the air pressure on the top of the column and restores the flow of eluant. The unit will collect three separate fractions from each column. A mechanical rack moves for this purpose three vials successively into place below the column, after preset volumes of eluant are collected, and only when eluant drops have stopped falling. Another original feature of the robot system at SAL is the trapping of RuO_4 evolved during the heating of the samples into paraffin oil (46).

The safety of the design was reviewed with IAEA and Austria Safety Experts (49). Cold tests of the various modes of operation (48) started in the last quarter of 1990. The general lay-out of the robotized system is shown on Figure 7.

FIG. 7 : Layout of Input-robot Glove-Box approx. to scale
1: 10.



Key to Fig. 7

1. Stand for glass tubes (Fission Products)
2. Stand for glass tubes (Pu)
3. Stand for glass tubes (U)
4. Stand for penicillin vials
5. Valency adjustment glass tube stand
6. Stand for glass tubes (liquid smoke)
7. Rabbit vials stand
8. Syringe stand
9. Vortex Mixer
10. Screw Cap station
11. Solid waste flask
12. Wet waste flask
13. Pipette-tip stand
14. RuO₄ trap-flask
15. Sliding door to Hot-plate chambers
16. Liquid waste pump
17. Pump for F.P. Hot plate air blower.
18. Pump for Pu & U Hot plate air blower.
19. Hot plate for samples containing Fission Products
20. Hot plate for Pu fractions
21. Hot plate for U fractions.
22. & 23. Access corridors
- H1. Grip Finger Hand for contaminated objects
- H2. Grip Finger Hand for clean objects
- H3. Pipette Hand
- H4. Syringe Hand

4.2.3. Hybrid K-edge absorptiometer/Fluorescence Analyzer

The instrument was moved to its permanent operating position in March 1990. Unstable count rates and poor resolution, especially in the fluorescence channel, were observed when resuming measurements. A service of the Link pulse processors, suspected to be faulty did not eliminate major noise pick-up problems. A Link expert finally cured it by grounding various casings with very thick braided conductors.

At the recommendation of IAEA and Austrian experts, a few additional safety devices were installed before overnight unattended measurements with plutonium samples were done.

Calibration parameters were determined for the absorptiometry of pure solutions of uranium, thorium and plutonium nitrate, using 2 and 4 cm cell paths. Only the fluorescence analysis of plutonium was calibrated, using uranium as internal standard.

Emphasis was put on the evaluation of the characteristics of the absorptiometry channel, which provides the reference measurement for plutonium K X-Ray fluorescence analysis in many mixed U/Pu materials. Unsufficient beam collimation can introduce large deviations from linear calibration. The effect increases with the cell path. With tight beam collimation (ϕ 1mm x L 100 mm) the non linearity with the 4 cm cell is reduced to \pm 0.5%. After a parabolic fit of the calibration data, the residuals have a relative standard deviation of 0.06% only (49).

4.2.4. X Ray Fluorescence Analysis of Uranium and Thorium Oxides

L. Wawrzonek had demonstrated in 1989 that he was able to reach a repeatability of 0.28% using the procedure he had developed for the preparation of glass beads containing 2% of uranium, and measuring with an energy dispersive XRF analyzer (50). The investigations continued in 1990 with mixtures of uranium and thorium oxides simulating MOX powders with U/Th ratios varying between 1/1 to 1/3. With a constant dilution factor ($D = 19.20 \pm 0.05$) the precision of the measurements and the repeatability of the preparation are about equal; their combined effects give a reproducibility of 0.5% for uranium, and 0.4% for thorium (51). A polyphosphate flux was also tested successfully as an alternative to borax fluxes, in case boron would not be acceptable in certain fuel fabrication plants (52).

L. Wawrzonek completed in June 1990 his 18 month research fellowship programme by analyzing a number of actual uranium oxide samples against synthetic standards. The mean relative difference between the XRF results and titration results was equal to -0.16% with a standard deviation of 0.52%. The repeatability of replicate preparations and measurements of the same sample had a coefficient of variation of 0.27% (53).

A Philips Automatic X-Ray Fluorescence Analyzer, model PW 1480, was selected for purchase in November 1990. Its delivery in SAL was expected for February 1991.

4.3 Treatment of Alpha Active Wastes

During the course of analytical operations at the Pu laboratory at SAL, about 300 liters of waste solutions containing plutonium with a concentration up to 0.15g/l, routinely arise yearly. Because of restrictions on the volume and content of α active liquid effluent for transfer from SAL to the Austrian Research Center of Seibersdorf (OFZS), and the cost of transporting such liquids elsewhere, there is a need to develop a mean of treating the solutions to provide a more concentrated active waste for transport and leaving an effluent suitable for treatment and disposal by OFZS.

J. Moreno reported a number of preliminary tests on synthetic wastes and suggested to investigate further two approaches (54): the simultaneous absorption of Uranium and Plutonium on a solvent extraction Chromatographic (CEC) column loaded with Tri-n-Octyl-Phosphine Oxide (TOPO), followed by coprecipitation of Ce(III) and Am(III) with oxalate or their absorption on a CEC loaded with CMPO were the approaches retained for further investigation because they are expected to minimize the final volumes of liquid wastes.

Further on U. Wenzel investigated the behaviour of plutonium of actual SAL liquid wastes on the extraction columns studied previously by Mr. Moreno. U. Wenzel concluded that it was worthwhile to set up a pilot separation unit containing devices for flow control, in line analysis and feed adjustment (55).

5. Training of Safeguards inspectors on Off-Site and On-Site Destructive Analysis

As in previous years two groups of about 12 Safeguards inspectors newly appointed by the IAEA attend a two days training: a one day lectures at VIC and a one day visit at SAL. They are informed on the role and the use of destructive analysis in the system of the IAEA Safeguards. They are instructed to witness the sample taking into suitable vials and the conditioning of the samples at the plant following qualified procedures in view of their analysis at SAL. The principles and the performances of the analytical techniques used at SAL are demonstrated and described. The choice and the use of shipping containers adequate to the type of radioactive materials, to its composition and to its amount are also presented and discussed in the framework of the transport regulations in force. At the end paired comparison evaluation of Operator-Inspector results are presented, compared to the ESARDA Target Values and discussed as well for each type of samples analyzed.

There was this year no course for experienced inspectors, but intensive discussions were held instead with the inspectors on duty at spent fuel reprocessing plants.

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AL-Documents

AL/28

Preparation and Provisional Validation of a Large Size Dried Spike:
Batch SAL-9931
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May 1990

AL/29

Preparation and Provisional Validation of a Large Size Dried Spike:
Batch SAL-9934
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Optimization of the Semiautomated MacDonald and Savage Procedure
V. Kuvik, L. Vrbova
June 1990

IR-Documents

SAL-IR 1/90

An Anionic Exchange Separation prior to Mass Spectrometric
U to Pu ratios up to 20).
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March 1990

SAL-IR 2/90

The SAL Decay Model for U/Pu/Am Mixtures.
H. Aigner, S. Deron
April 1990

SAL-IR 3/90

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Packing for Shipment
H. Swietly
May 1990

SAL-IR 4/90

The Scaled Down MacDonald-Savage Potentiometric Titration Adapted for a
Routine Automatic Analysis of Plutonium Mg Sized Safeguards Samples
V. Kuvik, N. Doubek et al.
April 90

List of publications, cont'd

SAL-IR 5/90

Experience in SAL with Plutonium Isotopic Analyses in Small Samples of Pu and U/Pu Products using HRGS/MGA2;

A preliminary report

S. Deron et al.

April 1990

SAL-IR 6/90

Evaluation of a Special Experiment to determine the Error in the Preparation of a Uranium Reference Solution

H. Aigner, S. Deron, M. Golbs, S. Berger

June 90

SAL-IR 7/90

Safety Analysis Report for the Input Lab. Robot

P. Zahradnik

March 90

SAL-IR 8/90

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April 90

SAL-IR 9/90

Characterisation of a Yellow Cake Powder

M. Golbs, H. Aigner, A. Zoigner, J. Parus, G. Bagliano

July 1990

SAL-IR 10/90

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U. Wenzel

September 1990

SAL-IR 11/90

IDMS analysis control at SAL and NWAL's using Large Size Dry Spike Batch LSD2. Evaluation and Exercise.

H. Aigner, A. Zoigner, N. Doubek

November 1990

STR-Documents

STR-259

The Use of Large Size Dried Spike for Accountability Measurements of Reprocessing Input Solutions.

E. Kuhn, S. Deron et al., PNC-TRP, NMCC-SAL

June 1990

List of publications, cont'd

Miscellaneous

Destructive Analysis: A Tool for Safeguards.

S. Deron

Contribution to IAEA Yearbook 1990

List of duty travels and their objectives, 1990, SAL

R. Fiedler

Almelo, Netherlands, 22 - 30 Jan. 1990
On-Site Verification Measurements of UF₆.

S. Deron

WAK, Karlsruhe, Germany, 6 - 7 Feb. 1990
Discussion of operator-inspector differences.

J. Parus

Ecublens, Switzerland, 27 - 28 Feb. 1990
Test performance of XRay fluorescence analyzers.

S. Deron

Saluggia, Italy, 2 - 4 April 1990
Attend meeting of ISO on analytical methods in spent fuel reprocessing.

G. Jammet

NRI, Rez, CSFR, 25 - 26 April 1990
To discuss McDonald and Savage procedure for titration of 4mg sized Pu samples.

G. Jammet

Marianske Lazne, CSFR, 7 - 11 May 1990
Attend 12th Radiochemical Conference and present poster on automatic Pu titration.

S. Deron

CBNM, Geel, Belgium, 10 - 11 May 1990
Invited speaker to 30th Anniversary of CBNM.
(No cost to the Agency)

N. Doubek

NMCC, PFPF Tokyo (Tokai-Mura), Japan, 17 - 30 June 1990
Assist in preparation of Large Size Dried Samples (LSD) for accountability assays of U and Pu in spent fuel solutions and their verification.

J. Gaensbacher

Gomel, USSR, 3 - 15 Sept. 1990
Participation in the Agency's project "The radiological consequences in the USSR from the Chernobyl accident: assessment of health and environmental effects and evaluation of protective measures" (Whole Body Group).

J. Capps

All Union Scientific and Research Institute, Moscow, USSR, 15 - 19 Oct. 1990
23rd meeting of ISO on analytical methods for the accountability of fissile materials in spent fuel reprocessing.

A. Zoigner

COGEMA Marcoule, FBFC Pierrelatte, France, 5 - 9 Nov. 1990
Preparation of samples for the qualification of sample bottles.

R. Fiedler

CBNM, Geel, Belgium, 19 - 22 Nov. 1990
To discuss fabrication and results of tests with CBNM of Large Size Dried Spikes for Isotope Dilute Assay of spent fuel samples.
(No cost to the Agency)