

Application of DA-Methods at PSI for the Characterisation of Non- Irradiated and Irradiated Nuclear Materials

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DA-Techniques and Equipments at PSI

Sample preparation

Non irradiated samples

MW -MLS-1200

HP-Berghof

Heating under reflux

Irradiated samples (shielded cell)

HP-Berghof

Heating under reflux

Electrochemistry

Element content (U, Np, Pu), acidity

Metrohm, TITRINO

Non metal analysis

Determination of H, C, N, O

LECO TC-436 (O,N)

LECO RH-404 (H)

LECO WR-412 (C)

Mass spectrometry:

**Element content, isotopic composition, ICP-MS, VG-PQ2+
isotopic ratio, burn-up MC-ICP-MS, NEPTUN***

TIMS, A-900

GAM-442

Gas analysis, fission gas analysis

Liquid chromatography

Element content, kation-/anion-analysis DIONEX DX-300

Thermal analysis

Thermal decomposition, O/Me ratio Mettler, TGA-851

= in operation 3/2001

Bestimmung von Kohlenstoff, Sauerstoff und Stickstoff in Nitrid

Bestimmung von Sauerstoff und Stickstoff

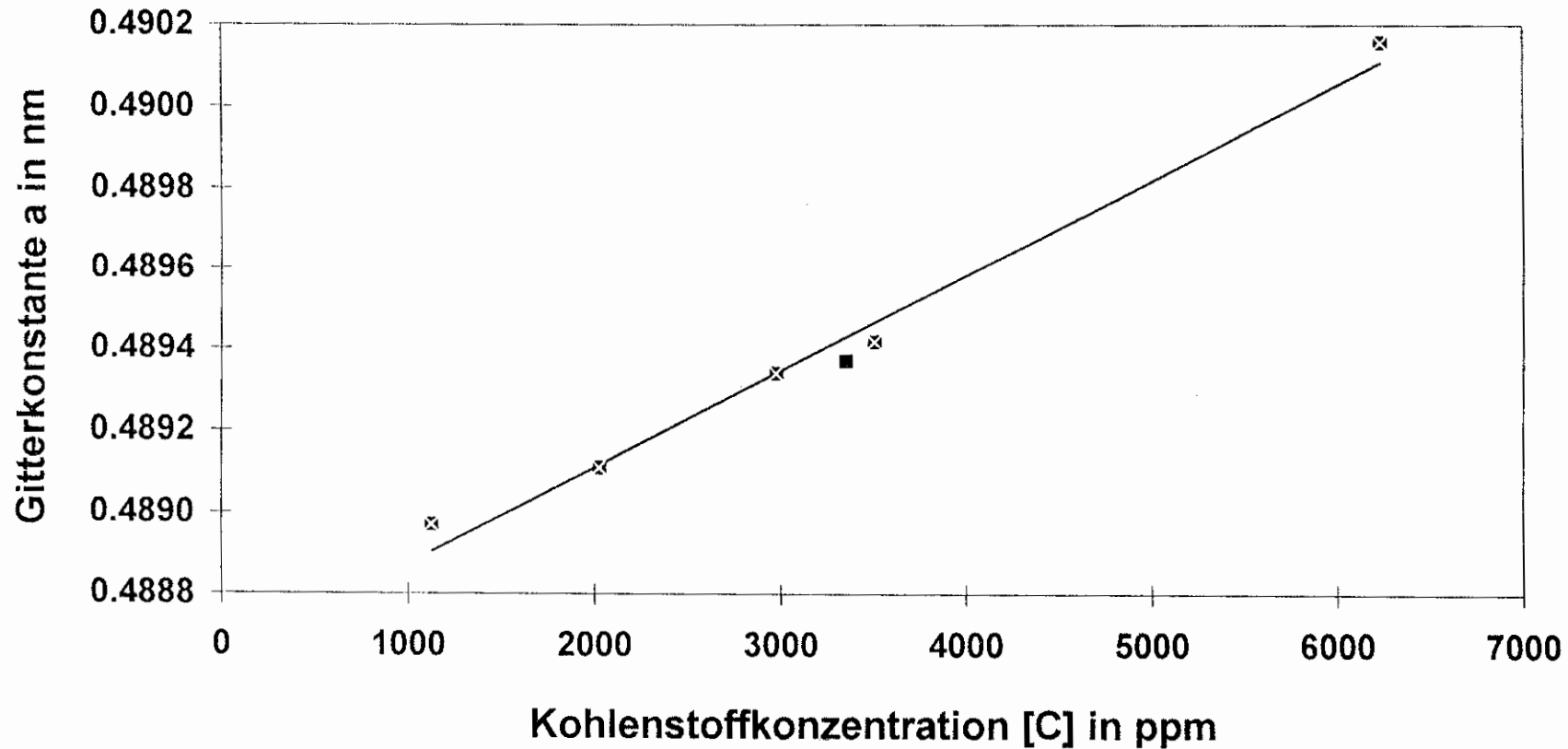
Messparameter TC-436:

Purge time:	15	s
Outgas pwr.:	1000	A
Analyze pwr.:	950	A
Graphit Tiegel	775-433/775-431	
Blank (1 Sn-Kapsel) N:	<0.1	ppm
O:	61±15	ppm

Abhängigkeit der Extraktion in Funktion der Temperatur (N-614)

Outgas pwr.	(A)	850	900	950	1000
Analyze pwr.	(A)	800	850	900	950
Temperatur	(°C)	1900	2000	2100	2200
Anzahl Analysen	(n)	4	10	20	8
Sauerstoff	(ppm)	625±90	671±106	646±43	578±41
Stickstoff	(ppm)	3.20±0.40	5.30±0.17	5.65±0.12	5.70±0.13

Änderung der Gitterkonstante a $U(N_{1-x}C_x)$ in Funktion der Kohlenstoffkonzentration [C]



O/M-ratio by thermogravimetry in sintered MOX

Thermoanalyser: Mettler TGA-851

- Resolution of balance
- Accuracy: 0.1 μg ;
 $\leq 1.0 \mu\text{g}$;
- Max. weight (UMT5): 1 g;
- Temperature range: RT -1100 °C;
0 °C;
- Oxygen potential (-100 kcal/mol) at:
(SHAW Moisture Analyser)
- Air 50 cm^3/min ;
- N₂ 50 cm^3/min ;
- Ar/H₂ (H max. 8 %) 50 cm^3/min ;

Method:

1. step: heating RT - 250 °C (50 °C/min); Atmosphere.: N₂ (50 cm³/min)
2. step: isoth. heating (30 min, 250 °C); Atmosphere: N₂ (50 cm³/min)
3. step: initial weight at 250 °C (W₁, ca. 100-200 mg)
4. step: heating 250 - 850 °C (50 °C/min); Atmosphere: air (50 cm³/min)
5. step: isoth. heating (130 min, 850 °C); Atmosphere: Ar/H (8%) (50 cm³/min)
6. step: cooling 850 - 250 °C; (~20 °C/min) Atmosphere: Ar/H (8%) (50 cm³/min)
7. step: isoth. heating (20 min, 250 °C); Atmosphere: N₂ (50 cm³/min)
8. step: final weight at 250 °C (W₂)

Calculations:

$$\frac{O}{M} = 2.000 - \frac{(W_2 - W_1) \cdot \frac{M_M}{M_O}}{W_1}$$

where: W₁ = initial weight; W₂ = final weight;

M_M = mol weight metal oxide; M_O = mol weight oxygen

Results:

	UO ₂ [*]	(U,Pu)O ₂	NpO ₂
1.	1.9862	1.9974	2.0046
2.	1.9821	1.9981	2.0072
3.	1.9615	1.9974	2.0045
4.	-	1.9979	-
mean	1.9766	1.9977	2.0054
s.d. (1 σ)	0.0132	0.0004	0.0015
r.s.d (%)	0.67	0.018	0.075

= preliminary test measurements, different method

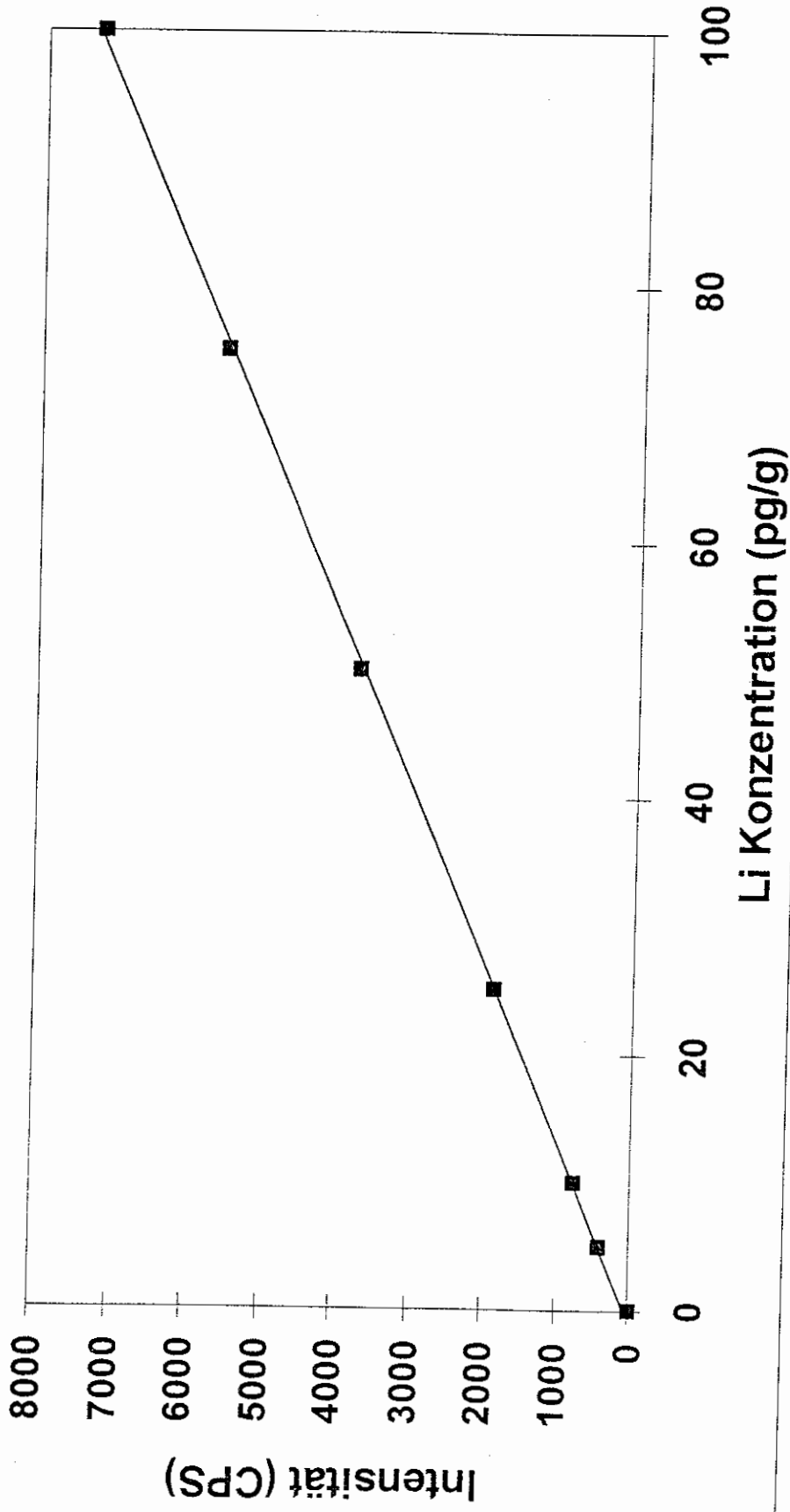
Glove-box version ICP-MS

- Extensive modifications of a commercial quadrupol ICP-MS instrument (VG PlasmaQuad PQ2+, Winsford, UK) had to be performed in order to provide the possibility of handling and measuring highly toxic and radioactive samples in a glove-box.
- The interface between the mass spectrometer and the torch-box is connected to the electro-polished stainless-steel glove-box with a special flange supplied by the manufacturer.
- The enclosures are required to cover the sample separation and introduction system (injection valve, separation columns, spray chamber and nebulizer, waste container), the torch-box and the work bench. All gas inlets into the glove-box, the vacuum line between interface and the rotary pump, and the ventilation inlet/outlet are equipped with absolute filters in order to prevent possible radioactive contamination of the environment.

Analysis procedure

- Leaching of adsorbed Li from surface and pores (boiling under reflux in A) H₂O; B) conc. HNO₃)
- Selective dissolution of Zircaloy in Br₂/CH₃CO₂CH₂CH₃
- Dissolution of the ZrO₂ - Layer in microwave oven with HF/H₂SO₄
- Quantitative analysis of Li with ICP-MS in:
 - A) leach solutions A) and B)
 - B) Zircaloy solution
 - C) ZrO₂ solution

Kalibrationskurve für Li-7



Resultate der Lithiumanalysen im Metall und in der Oxidschicht

	Blind	2601 D	2701 D	2701 J	2804 I	2804 P
Dicke der Oxid- schicht in μm		55	55	45	70	40
Leachlsg. A (ppm)	0.08 - 0.8	< 0.1	< 0.4	0.1	0.4	< 0.4
Leachlsg. B (ppm)	0.3 - 1.1	< 0.7	< 0.7	< 0.7	< 0.7	< 0.7
Oxidschicht (ppm)	0.7 - 1.4	36.2	66.4	22.3	35.5	20.6
Metallphase (ppm)		0.29	0.19	0.11	0.21	0.06
$\delta\text{Li}/7\text{Li}$ im Metall 0.081		0.081	0.089	0.073	0.084	0.104
$\delta\text{Li}/7\text{Li}$ im Oxid 0.081		0.009	0.011	0.009	0.013	0.018

ARIANE - International Programme

Actinides Research In A Nuclear Element

Motivation:

- Introducing a new and faster method at PSI for the burnup determination: Coupling a HPLC (element separation) with an ICP-MS (nuclide detection)
- Methods development for the accurate determination of a wide series of actinides and fission products
- Quality assurance by analyzing the same samples in different laboratories

Goal:

- To provide improved knowledge of the inventories of actinides and fission products in UO_2 and MOX fuels irradiated at various burnups for PWRs and BWRs

International Collaboration:

- International project managed by Belgonucléaire (participants: B, CH, D, JP, NL, UK, USA)
- Chemical analyses in three laboratories (ITU in Karlsruhe, SCK•CEN in Mol, PSI)

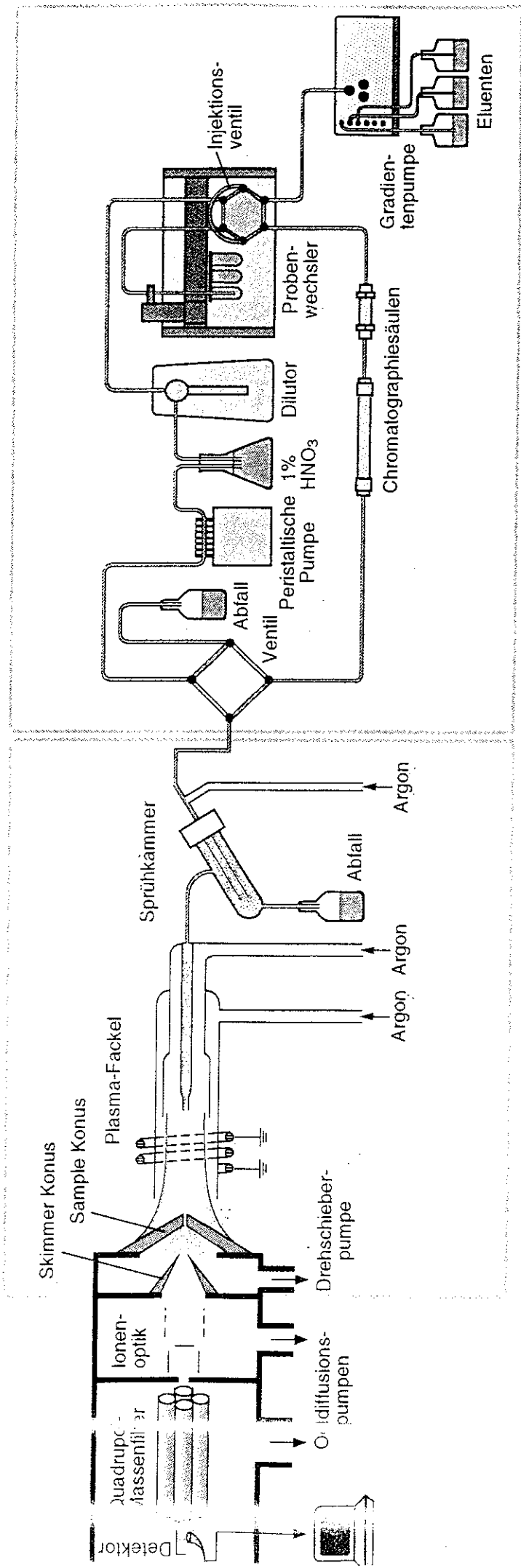
Results:

- Recommended and accurate values for nearly 50 nuclides in irradiated UO_2 and MOX fuel at different burnups (40 to 60 GWd/tM)
- ⇒ Improvement of the data base for the calibration of source term codes for high burnup conditions and MOX fuel recycling scenarios

Determination of the nuclear burn-up by HPLC-ICP-MS

- The determination of the burn-up in an irradiated nuclear fuel is an important parameter for the design and operation of nuclear power reactors.
- The experimental determination of the burn-up in an irradiated nuclear fuel is accomplished by analysing the number of uranium, plutonium and neodymium atoms. ^{148}Nd is used as burn-up monitor for the calculations.
- Numerous isobaric overlaps restrict the direct determination of actinides and fission products by mass spectrometry. Therefore, an extensive chemical separation for a number of elements is required.

- **Since the concentrations of these elements are determined by isotopic dilution analysis, the separation has to be done twice: once for the unspiked sample and once for the spiked sample.**
- **The classical methods involve extensive and very time-consuming separation steps for Nd, U and Pu, resulting in a great risk for contamination of the sample and a high radioactive dose for the operator.**
- **Therefore, high-performance liquid chromatography (HPLC) technique, coupled on-line with an ICP-MS is used in our laboratory for the determination of nuclear burn-up as routine method.**



RS43-6B/K182

Separation of lanthanides and actinides in MOX fuel. chromatographic parameters (column: Dionex CS5)

Separation of the lanthanides

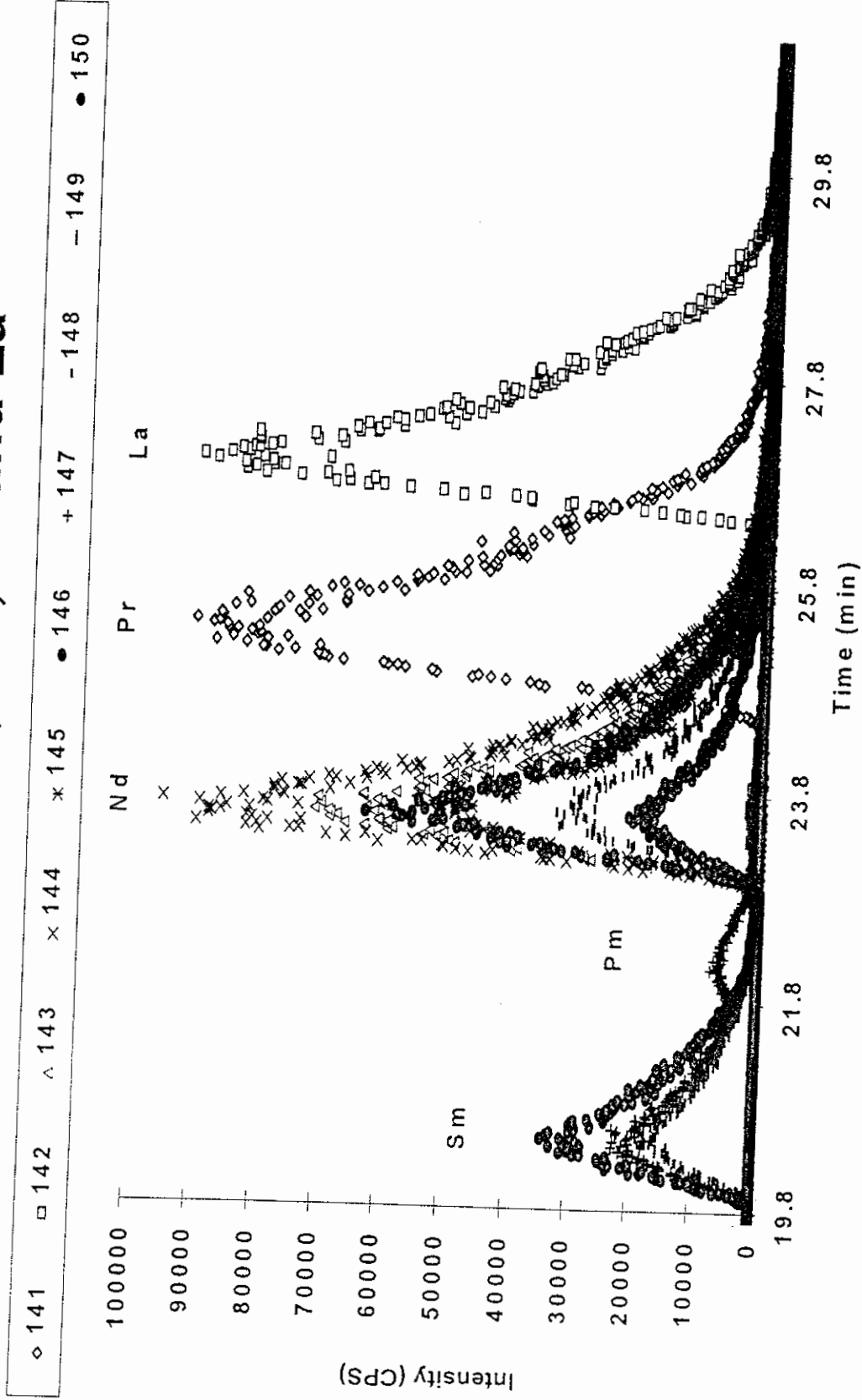
Time (min)	H ₂ O (%)	1 M HCl (%)	0.4 M HIBA ¹⁾ (%)
0	0	100	0
0.1	90	0	10
8.0	90	0	10
26.0	35	0	65

Separation of uranium and plutonium

Time (min)	H ₂ O (%)	2 M HNO ₃ (%)	1 M HCl (%)	0.4 M HIBA ¹⁾ (%)
0	80	20	0	0
1.5	80	20	0	0
1.6	0	0	100	0
4.0	0	0	100	0
4.1	35	0	0	65
15.0	35	0	0	65

1) = α - hydroxy-isobutyric acid (HIBA)

Separation of Nd from Sm, Pm, Pr and La



Determination of the nuclear burn-up

$$FIMA = \frac{N_F}{N_M^0}$$

where: FIMA (fission per initial metal atoms) = burn-up

N_F = number of fissions; N_M^0 = number of initial atoms

- › Absolute values for the burn-up of nuclear fuel samples may not be presented in this paper due to an agreement between PSI and the participants of the project.
- › Comparative measurements of the burn-up between the classical TIMS technique and the newly developed HPLC-ICP-MS show that the results obtained have a comparable accuracy. However, considerable differences are found comparing the precision of the data.

Comparison with the multi-collector systems

- In the classical burn-up determination technique the isotopic composition of the elements is usually measured (TIMS). The advantages of TIMS are: 1) a very stable ionisation process; and 2) the possibility to perform simultaneous measurements of each isotope of the element using a series of Faraday cup detectors.
- The limitations of the quadrupol ICP-MS method are the higher instability of the ionisation process in the plasma and the sequential measurement technique using only one detector.
- In order to compare the performance of the different mass spectrometric methods for the determination of the uranium composition two uranium solutions with different isotopic composition were prepared using an IRMM-040a ^{233}U spike solution, IRMM-110 (UO_2) reference material and NBS-U-500 (U_3O_8) standard: $^{233}\text{U} : ^{235}\text{U} : ^{238}\text{U} = 1 : 1 : 1$ and $^{233}\text{U} : ^{238}\text{U} = 1 : 2$.

Determination of the isotopic composition of an uranium standard mixture $^{233}\text{U} : ^{238}\text{U} \approx 1 : 2$.

	^{233}U	^{234}U	^{235}U	^{236}U	^{238}U
	at. (%)	at. (%)	at. (%)	at. (%)	at. (%)
calc. val.	35.1291	0.3289	0.2822	0.0174	64.2424
TIMS ETHZ	35.0598	0.3279	0.2843	0.0175	64.3105
st. dev. (1s)	0.0009	0.0001	0.0001	0.0001	0.0012
Q-ICP-MS	35.4459	0.3359	0.2976	0.0169	63.9037
st. dev. (1s)	0.0756	0.0368	0.0206	0.0130	0.0058

* data are kindly provided by Dr. F. Oberli, ETH Zürich

Nevertheless, the founded loss of precision in the ICP-MS approach compared with TIMS is more or less compensated by the considerable time-saving for the sample preparation and the analysis.

The development of a new generation of instruments, so-called MC-ICP-MS systems, equipped with ICP ionisation source and magnet-sector mass spectrometer with up to 12 Faraday cups as detectors, make possible the simultaneous measurement of all important isotopes of an element. The results obtained look very promising in respect to the accuracy and precision of the data. This new type of instruments offers the opportunity to achieve data in the same quality as TIMS but with all analytical benefits as known from ICP-MS.