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BURNUP DETERMINATION OF A FUEL STRING

BY CHEMICAL AND ISOTOPIC ANALYSIS

by

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Summary

The burnup of six fuel bundles irradiated in NRU
was determined by chemical and isotopic analysis. The
concentration of uranium and plutonium in solution was
determined by controlled potential coulometry and 2π alpha
counting respectively. Alpha spectra obtained from sub-
limed plutonium sources provided the $^{238}Pu/^{239}Pu + ^{240}Pu$
ratios needed for corrections.

Mass spectrometric analyses were done on separated
uranium and plutonium solutions. The number of uranium and
plutonium fissions were calculated from the ^{235}U depletion
and the Pu/U ratio.

Détermination de taux de combustion d'un train de combustibles par analyse chimique et isotopique

par

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Résumé

Les taux de combustion de six grappes de combustible irradiées dans le NRU ont été déterminés par analyse chimique et isotopique. Le dosage d'uranium en solution a été déterminé par coulométrie à potentiel contrôlé tandis que celui du plutonium par taux de comptage en se servant d'un compteur alpha 2π, balayé au gaz méthane. Ce taux a été corrigé en mesure du rapport $^{238}Pu/^{239}Pu + ^{240}Pu$ effectué par spectrométrie alpha.

L'analyse isotopique de l'uranium et du plutonium par spectrométrie de masse à thermoionisation a fourni les données nécessaires pour calculer le nombre de fissions d'uranium par la décroissance de ^{235}U et, avec le rapport Pu/U, le nombre de fissions de plutonium.

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Introduction

The chemical and isotopic analysis of six fuel bundles
of different enrichments and irradiations was required by the
Nuclear Fuels Engineering Branch. This report presents the
details of the analytical work done by the General Chemistry
Branch.

Sampling and Preparation

Four pellets were taken from each bundle at mid plane
on a diameter representing a cross section of the bundle, two
pellets from the outer and opposite elements, one from the
inner and one from the center elements as shown in Fig. 1.
Sampling was done in the CRNL Universal Cells.

The twenty-four pellets so obtained were dissolved,
under reflux, individually in hot concentrated nitric acid. The
solutions were then adjusted to 7.5 M nitric acid with dilute
nitric acid. The dissolutions were done in the General Chemistry
Branch's hot cell.

Uranium Analysis

Uranium was determined by controlled potential coulo-
metry using an ORNL Model Q-2005X50 coulometer. The charge on the
current integrator was read with a digital voltmeter accurate to
0.01 mV while a strip chart recorder traced the titration current.

The uranium was reduced at the surface of a controlled mercury electrode in a titration cell as shown in Fig. 2. The mercury and the sample to be analyzed were added to the 37 mm x 75 mm Pyrex cell. An inlet tube for the helium cover gas, and two barrier tubes in which the other electrodes were placed, were fitted to the Teflon cover. These barrier tubes were 8 mm Pyrex tubing with a glass frit at one end constructed as described by Bird (3).

A hot mixture of 3% Agar-agar and 5% potassium sulfate was poured into these barrier tubes forming a 6 mm thick gel at the bottom on cooling. The isolated electrode, a coil of 1 mm platinum wire, and the reference electrode, a Standard Calomel Electrode, were placed in these tubes, which were filled with 0.5 M sulfuric acid. The working electrode consisted of 7.3 ml of mercury, the surface of which was continuously renewed by a Teflon disk, spun at a rate just below that at which the mercury would break up into droplets. The whole titrating cell was flushed continuously with humidified helium gas. Helium flushing was carried out for 5 to 10 minutes before each reduction.

Prior to the uranium analyses, the triple distilled mercury electrode was conditioned by titrating 10 ml portions of 2 M sulfuric acid until a negligible blank was obtained. Standards were run with every set of samples. Triplicate samples weighed on a microbalance were taken from each solution and placed in 100 ml beakers. These were fumed three times with sulfuric acid, then transferred to the titration cell with 10 ml of 2 M sulfuric

acid. For the first fuming 0.25 ml of perchloric acid and 0.5 ml of concentrated sulfuric acid were added to the samples. It was important to wash down the sides of the beakers with distilled water between each fuming to make sure that all the perchloric acid was driven off. One drop of concentrated sulfuric acid in addition to the distilled water was added to each of the two succeeding fumings. Iron and other impurities were pre-reduced at a potential of +0.08 V followed by the reduction of U(VI) to U(IV) at a final potential of -0.325 V, approached in such a manner that the cell current did not exceed 60 mA. It was also observed that if the uranium samples had not been properly fumed, the pre-reduction was high and the U(VI) to U(IV) titer had a tendency to tail. The uranium concentration was calculated using the following equation:

$$\text{Weight of Uranium} = \frac{V \cdot C}{2 \cdot F \cdot A} \qquad [1]$$

where V is the reading in volts as recorded on the digital voltmeter and corrected for Faraday currents and the blank;

C is the integrator constant in coulombs per volt obtained by applying a known potential across a fixed precision resistance for a given time and noting the charge on the integrator;

F is the Faraday;

A is the atomic weight of the analyzed uranium.

A 3 mg sample was normally determined with a precision of ±0.2%.

Plutonium Analysis

Plutonium was determined by α counting following separation from uranium and fission products. A 2π methane flow α proportional counter was used for this determination.

Triplicate samples of the solutions were weighed and allowed to evaporate slowly to dryness in order to drive off all the concentrated nitric acid. The residues were then taken up in 1 ml of 0.5 M nitric acid and 0.25 ml of 15% hydroxylamine nitrate solution and let stand approximately 16 hours during which time all the Pu(IV) and Pu(VI) was reduced to Pu(III). The hydroxylamine nitrate was destroyed and the plutonium was oxidized to Pu(IV) by the addition of concentrated nitric acid to the hot solutions. The nitric acid concentration was adjusted to 7.5 M. The samples were then applied immediately to chromatographic columns. These small 4 mm x 50 mm Dowex 1 x 4, 200-400 mesh resin columns had been pre-conditioned with 7.5 M nitric acid. Under these conditions the Pu(IV) was adsorbed by the resin while the uranium and fission products were not. A 7.5 M nitric acid wash removed the latter completely from the column. The plutonium was eluted with 0.5 M nitric acid. A hydroxylamine nitrate wash solution reduced all remaining traces of plutonium in the column to Pu(III). Thus it was removed from the column since Pu(III) is not retained by the resin. This eluate was heated, treated with

concentrated nitric acid to destroy the hydroxylamine nitrate, and combined with the first eluate. Weighed samples of these solutions were deposited on polished stainless steel disks, dried and counted in a 2π methane flow proportional counter standardized with a plutonium source counted in a low geometry methane counter.

The relative contributions of the ^{238}Pu, ^{239}Pu and ^{240}Pu α-emitting isotopes were obtained by α spectrometry of very thin sources. One drop of separated and purified plutonium solution was dried under vacuum on a tungsten filament heated by a very low current. Volatile salts were vaporized by heating to approximately 500°C and the plutonium was sublimed onto stainless steel disks by heating to white heat for a few seconds (cf. Fig. 3). These thin sources were then counted using an Ortec surface barrier silicon detector with a FET (Field-Effect-Transistor) pre-amplifier. Pulses were analyzed with a Chalk River nuclear spectrometer using a PDP-8 (Digital Equipment Corp.) computer. The quality of the detector's resolution can be seen on the spectrum, Fig. 4, where the full width at half maximum of the 5.499 MeV α peak was 14 keV.

Uranium and Plutonium Isotopic Analysis

The isotopic analysis of purified uranium and plutonium solutions was carried out on two thermionic source mass spectrometers (Consolidated Electrodynamics Corp. Model 21-702B and Model 21-703). Uranium was extracted from samples of the original solutions of pellets with 20% tributyl phosphate in

xylene. A 5 M nitric acid wash followed by several hydroxylamine nitrate washes removed the fission products and all traces of plutonium. The uranium was recovered by washing the organic phase with distilled water.

Plutonium from samples of the solutions was adsorbed on Dowex 1 x 4, 200-400 mesh resin columns. The uranium and fission products were removed by washing the columns with 7.5 M nitric acid. The plutonium was eluted with 0.5 M nitric acid.

Calculations for the Number of Fissions

Equation [2] was used to calculate the number of ^{235}U fissions:

$$F_5 = N_{5(o)} \ (1-R_w\Delta/R_o) \ \hat{\sigma}_{f_5}/\hat{\sigma}_{a_5} \qquad [2]$$

where $N_{5(o)}$ is the number of initial ^{235}U atoms

R_w is the final $^{235}U/^{238}U$ ratio

R_o is the initial $^{235}U/^{238}U$ ratio

Δ is a correction for ^{238}U depletion

$\hat{\sigma}_{f_5}$ is the ^{235}U fission cross section

$\hat{\sigma}_{a_5}$ is the ^{235}U absorption cross section

The irradiation ϕt (integrated flux n/kb) was obtained from the uranium isotopic analyses using equation [2a]:

$$\frac{R_w\Delta}{R_o} = \exp - [\hat{\sigma}_{a_5}\phi t] \qquad [2a]$$

The number of ^{239}Pu fissions was obtained using equation [3]:

$$F_9 = \frac{N_{5(o)} \cdot N_{Pu}/N_u \; (\varepsilon) \; [A_o + A_1 + A_2 \; (1 + 1/\alpha_1)]}{R_o \cdot \alpha_9} \qquad [3]$$

where ε is a correction for ^{235}U and ^{238}U depletion. This is equal to the ratio of the final atoms of all the uranium isotopes to the initial ^{238}U.

α_9 and α_1 are the capture to fission ratios for ^{239}Pu and ^{241}Pu respectively.

N_{Pu} and N_u are the final total Pu and U concentrations.

A_o, A_1, A_2 are the Pu isotopic fractional abundances.

The number of ^{241}Pu fissions was obtained using equation [4]:

$$F_1 = \frac{N_{5(o)} \cdot N_{Pu}/N_u \; (\varepsilon) \; (A_2)}{R_o \cdot \alpha_1} \qquad [4]$$

The number of ^{238}U fissions was obtained using equation [5]:

$$F_8 = (F_5 + F_9 + F_1) \; \delta \qquad [5]$$

where δ is the ratio of fast neutron fissions to thermal neutron fissions derived from experimental values obtained by C.B. Bigham (5) for 28 element bundles.

The effective cross-section ratios and capture-to-fission ratios were calculated from C.H. Westcott's (6) compilation.

The epithermal index values and neutron temperatures were estimated using Bigham et al (7) experimental values. The total number of fissions per kg of U was converted to total energy produced using 199 MeV per fission (3.69×10^{-22} MWd per fission).

Table I is a summary of the isotopic analyses done by mass spectrometry. Table II is a summary of the uranium and plutonium analyses expressed as the Pu/U weight ratio. This table also shows the alpha spectrometric analyses and the final results expressed as the integrated neutron flux and the burnup. The figures in brackets were estimated since in this case some uranium solution was lost during fuming due to too rapid a rise in the temperature.

Acknowledgements

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*AECL-XXX: report published by Atomic Energy of Canada
Limited.

TABLE I

Mass Spectrometric Results

Sample		Uranium 235/238 Atom Ratio		Plutonium Atom Percent			
		Initial	Final	239	240	241	242
U219	RRA 2	.01270	.00865	85.96	12.43	1.489	.117
U219	RRA10	.01270	.00889	83.16	12.32	1.443	.115
U219	RRA17	.01270	.00989	89.19	9.69	1.060	.056
U219	RRA25	.01270	.01050	91.03	8.10	.828	.035
U210	RSA 2	.01510	.01111	88.26	10.52	1.150	.070
U210	RSA10	.01510	.01116	88.44	10.36	1.125	.072
U210	RSA17	.01510	.01236	91.29	7.00	.771	.033
U210	RSA25	.01510	.01297	92.67	6.70	.613	.020
U210	RZA 2	.01270	.00937	88.84	10.04	1.055	.065
U210	RZA10	.01270	.00931	88.69	10.15	1.085	.068
U2 0	RZA17	.01270	.01040	91.51	7.72	.736	.028
U210	RZA25	.01270	.01081	92.79	6.61	.590	.010
U210	SAA 2	.01668	.01429	93.85	5.78	.363	.011
U210	SAA10	.01668	.01418	93.66	5.95	.377	.015
U210	SAA17	.01668	.01512	95.44	4.32	.241	0.000
U120	SAA25	.01668	.01550	96.23	3.57	.188	0.000
U209	SBA 2	.01510	.01147	89.90	9.20	.859	.050
U209	SBA11	.01510	.01151	89.62	9.41	.906	.060
U209	SBA17	.01510	.01266	92.37	7.02	.603	0.000
U209	SBA25	.01510	.01319	93.70	5.83	.470	0.000
U210	TNA 5	.01282	.00733	80.06	17.03	2.590	.319
U210	TNA13	.01282	.00745	80.31	16.81	2.570	.310
U210	TNA19	.01282	.00896	84.74	13.24	1.870	.150
U210	TNA26	.01282	.00973	87.33	11.06	1.520	.090

TABLE II

Summary of Final Results

Sample		α Ratio $^{238}Pu/^{239}Pu$ $+ ^{240}Pu$	Weight Ratio Pu/U	Irradiation Integrated Flux n/kb	Burnup* KWD/Kg U
U219	RRA 2	.07184	1.993E-03	.597	3870
U219	RRA10	.07126	1.981E-03	.554	3670
U219	RRA17	.06366	1.632E-03	.388	2700
U219	RRA25	.05854	1.434E-03	.295	2110
U210	RSA 2	.05692	1.742E-03	.477	3660
U210	RSA10	.05775	1.731E-03	.470	3610
U210	RSA17	.05235	1.430E-03	.311	2500
U210	RSA25	.04876	1.239E-03	.236	1970
U210	RZA 2	.04906	1.707E-03	.472	3100
U210	RZA10	.05011	1.795E-03	.482	3170
U210	RZA17	.04521	1.388E-03	.310	2150
U210	RZA25	.04306	1.261E-03	.250	1770
U210	SAA 2	.03111	1.061E-03	.240	2070
U210	SAA10	.03283	1.077E-03	.252	2170
U210	SAA17	.02867	8.419E-04	.152	1370
U210	SAA25	.02637	7.350E-04	.114	1040
U209	SBA 2	.04829	1.591E-03	.427	3280
U209	SBA11	.05014	1.632E-03	.422	3260
U209	SBA17	.04459	1.322E-03	.274	2230
U209	SBA25	.04125	1.154E-03	.210	1750
U210	TNA 5	.10970	2.658E-03	.869	5580
U210	TNA13	.10938	2.627E-03	.843	5460
U210	TNA19	.09710	2.173E-03	.556	3890
U210	TNA26	.08843	[1.910E-03]	.428	[3090]

* 199 MeV per fission

SAMPLED ELEMENTS
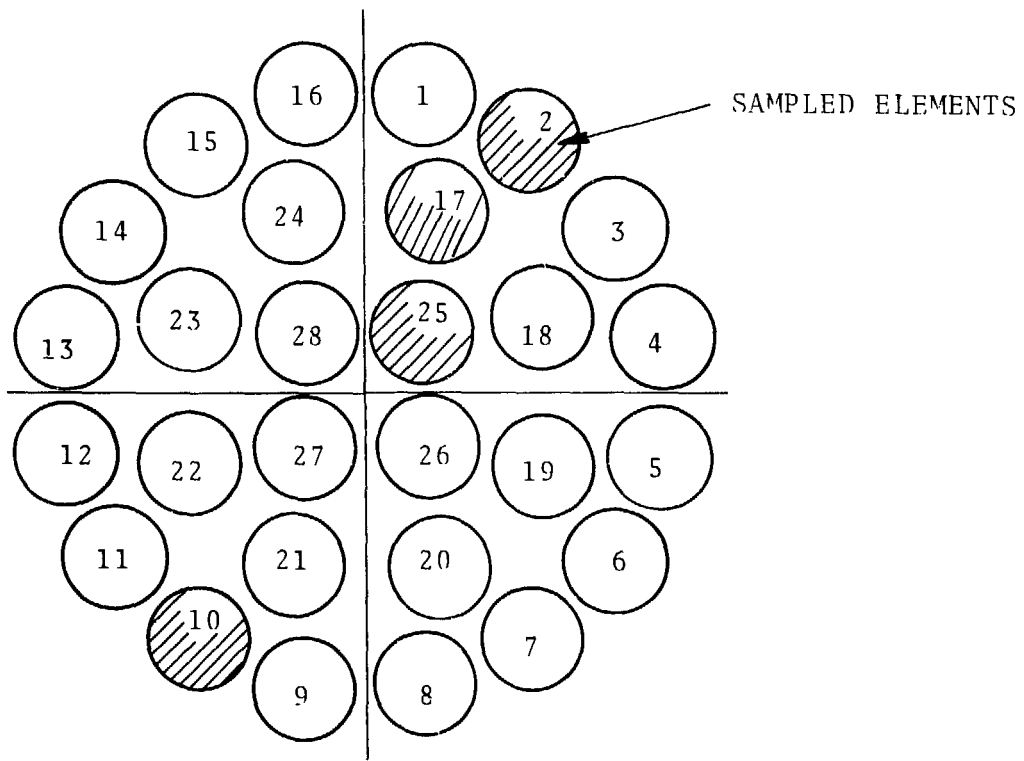
Fig. 1.   28 ELEMENT BUNDLE

Fig. 2. COULOMETRIC CELL

PLEXIGLASS COVER

VACUUM

S.S. DISK

SCREW

TUNGSTEN RIBBON

SAMPLE

SHOULDER

"TEFLON" SUPPORT

O-RING

THREADED STEEL ELECTRODE

SLEEVES

NUT

POWER LEADS
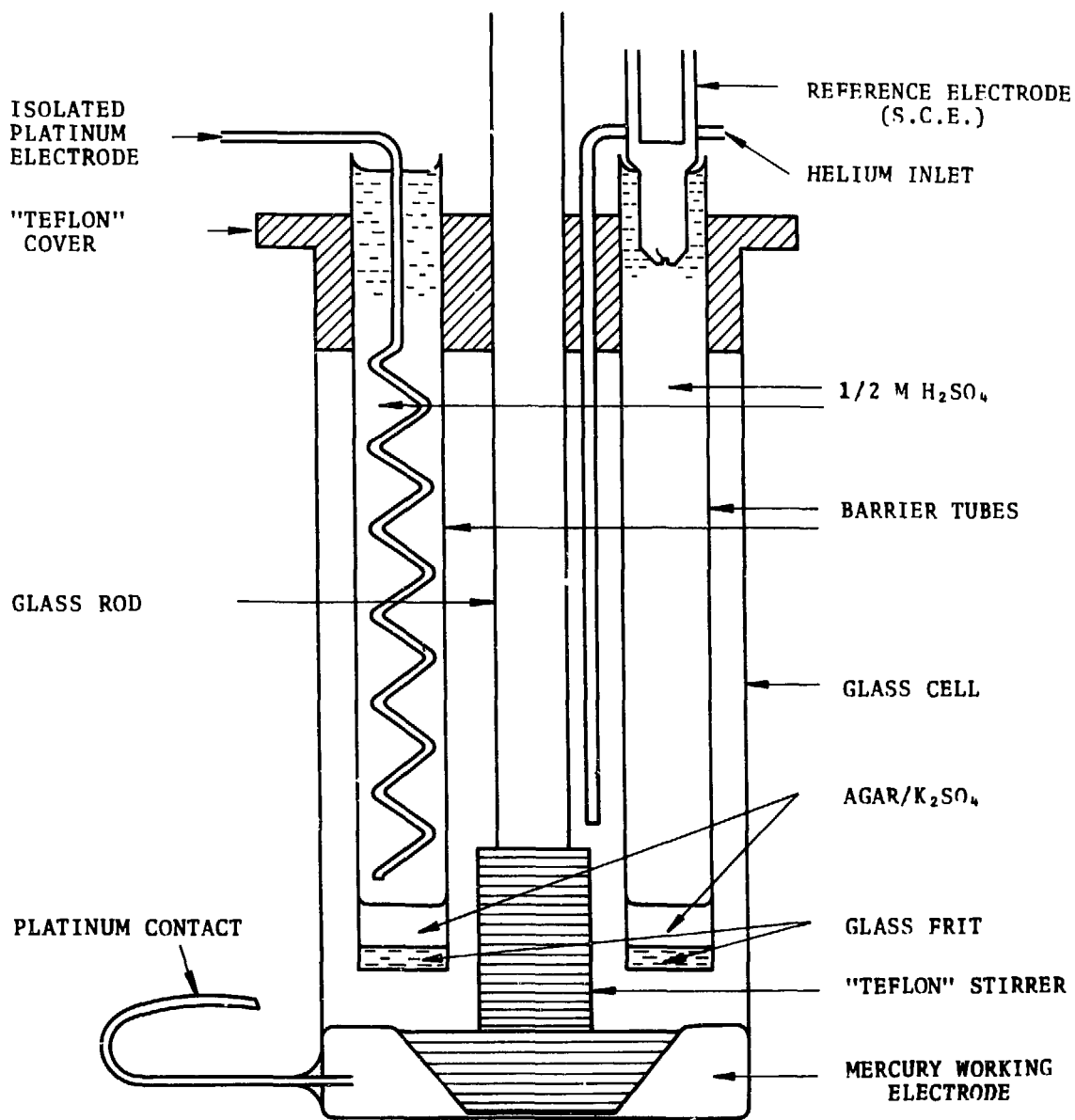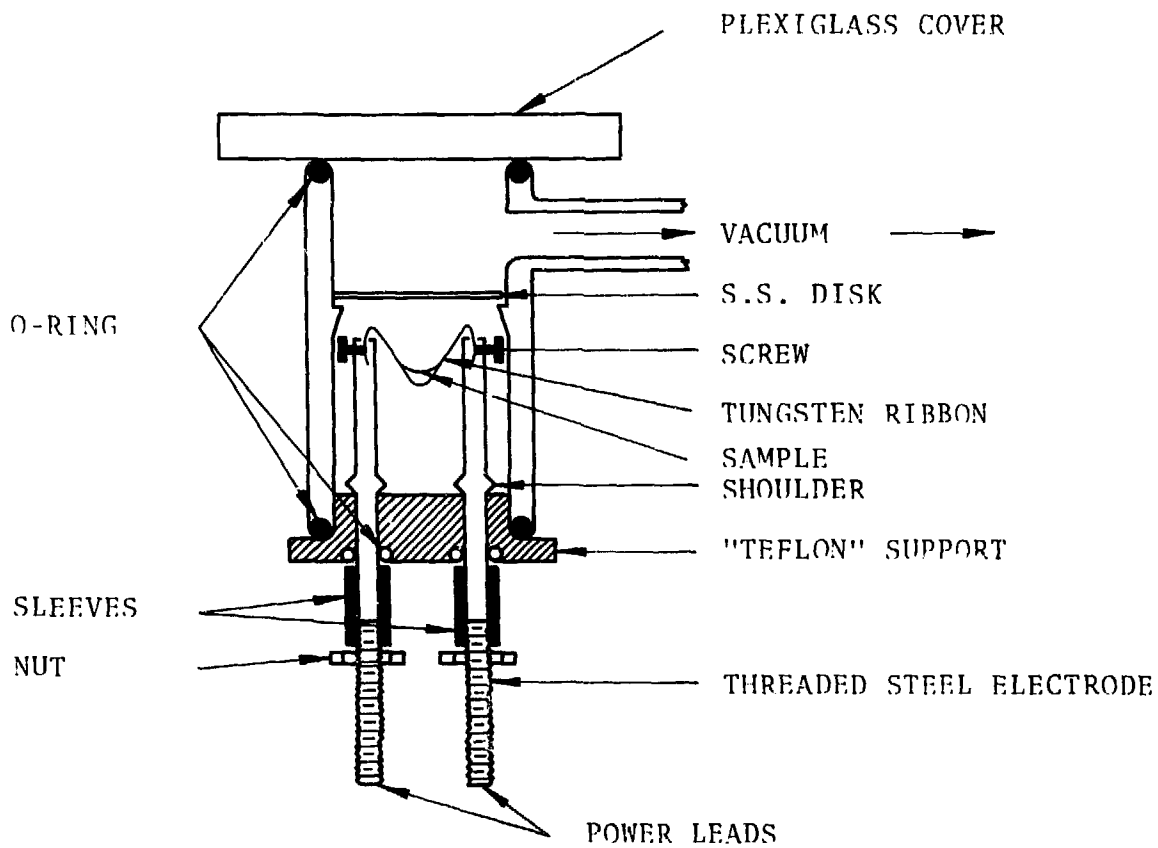
Fig. 3.   SUBLIMER USED TO PREPARE THIN SOURCES

COUNTS

10^5

10^4

10^3

10^2

^{239}Pu

^{240}Pu

^{238}Pu

5.157

5.145

5.168

5.107

5.123

5.456

5.499

525

625

725

825

CHANNEL

Fig. 4.   PLUTONIUM α SPECTRUM

278-73