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FABRICATION OF INERT MATRICES FOR HETEROGENEOUS TRANSMUTATION

EFTTRA-T2 (RAS 2) irradiation programme

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Abstract

This report describes the fabrication of targets containing inert matrices for the heterogeneous transmutation of plutonium and minor actinides. These targets will be irradiated in the EFTTRA-T2 (RAS-2) irradiation programme. The selection, preparation and characterization of the inert matrices and fabrication and loading of the irradiation capsules are discussed.

Keywords

inert matrices
transmutation
EFTTRA-T2
RAS-2

CONTENTS

1. INTRODUCTION

Partitioning and transmutation (P&T) of minor actinides is presently being studied as a complementary option in the management of high-level nuclear waste. It involves the separation of the actinides from spent fuel and subsequent re-irradiation to reduce the long-term radiotoxicity as well as the risk during storage. There is general agreement that the implementation of P&T in waste management is feasible but many technological issues have still to be solved. In Europe the EFTTRA-cooperation [1] has been initiated to study the technological aspects of transmutation of actinides and fission products.

Two ways are generally considered for the transmutation of the actinides: homogenous mixing in fresh fuel or heterogeneous mixing with a inert ceramic material. Homogeneous mixing can be considered as an adaption of mixed oxide fuel and can be implemented with minor modifications of present technology. However, due to dose limitations it cannot be used for americium fuels. Heterogeneous mixing is also attracting much attention at present as the amount of minor actinides formed during irradiation will be relatively low due to the absence of ^{238}U. However, new technology is required before implementation of this option can be achieved.

In the present document the preparation of samples of some selected inert matrix materials for the EFTTRA-T2 (RAS-2) irradiation in the High Flux Reactor (HFR, Petten) is described. The objective of this experiment is the study of the material behaviour (neutron-radiation damage) during in-pile irradiation. This experiment is performed in two different legs of a TRIO irradiation capsule [2] which contain almost identical sample holders (Figure 1). One sample holder will be irradiated during 4 HFR cycles, the other during 2 years, thus giving different total neutron doses.

2. SELECTION OF INERT MATRICES

The selection criteria for inert matrix materials is already discussed in detail by Konings [3]. The following table gives a summary of the properties of some oxide materials, which are the most promissing materials for use in a water cooled reactor.

	neutronics	thermal stability	irradiation behaviour	thermal conduct.	compatibility	fabrication
BeO	++	++	-	++	-	?
MgO	++	++	+	++	-	+
CaO	++	++	?	+	-	+
Al_2O_3	++	++	-	++	+/-	-
Y_2O_3	+	++	?	-	?	?
ZrO_2	++	+/-	+	-	++	++
CeO_2	+	+	?	?	++	++
$ZrSiO_4$	++	-	++	-	?	?
$MgAl_2O_4$ (spinel)	++	++	++	+	++	-
$Y_3Al_5O_{12}$ (YAG)	+	+	?	?	?	?

From above table four compounds were selected for investigation in the EFTTRA-T2 (RAS-2) irradiation programme. The selected materials are **Spinel, YAG, Al_2O_3 and CeO_2**. The following chapters discusses the fabrication, characterization of pellets made from these compounds and loading the pellets into the capsules.

3. FABRICATION AND CHARACTERIZING OF INERT MATRICES

3.1. Fabrication

3.1.1. Spinel

Spinel ($MgAl_2O_4$) was purchased from Gimex (Baikowski S28CR). Analytical analysis shows about 0.6% of free MgO. X-ray diffraction analysis did not reveal other impurities than MgO.

Because of the poor pressing properties the spinel powder was spray-dried to raise the grain size. A spinel suspension was made by mixing 50 g of spinel powder with 200 ml water and 1 ml of 3 molair nitric acid. The suspension was subsequently spray-dried in a Büchi mini spray dryer with an in- and outlet temperature of respectively 215 and 105°C.

The powder was pressed to pellets in a steel die at a pressure of 85 MPa. The pellets were subsequently sintered at 1600°C for 10 hours in air.

The pressing and sintering condition were choosen to result in pellets with a diameter of 9.0 mm so the pellets can be loaded in the irradiation capsule without furher mechanical operations.

3.1.2. YAG

YAG ($Y_3Al_5O_{12}$) was purchased from Gimex, with a typically purity of ≥99.9% and a grain size of 1 μm.

Pellets were manufactured by the ceramic workshop at ECN. The powder was first pressed to rods by cold isostatic pressing at 200 MPa. The rods were then presintered at 1000°C in air. After cooling down the rod was mechanically processed to the right diameter and cut into pellets. These pellets were finally sintered at 1600°C in air resulting in 9.0 mm diameter pellets.

3.1.3. Al_2O_3

These pellets were also manufactured by the ceramic workshop. First, the Al_2O_3 powder (ALCO CT3000sg, purity ≥99.7%, size <1 μm) was pressed to a rod by cold isostatic pressing at 200 MPa. The rod was presintered at 1000°C in air. After this preheating the rod is processed to the right diameter and cut into pellets which were finally sintered at 1600°C in air.

3.1.4. CeO_2

CeO_2 was purchased from Cerac, typically purity given by the vendor was ≥99.9%. The grain size was <50 μm.

To improve the pressing performance, the CeO_2 powder was mixed with a plasticizer (2 weight% Hoechst wax C micropulver PM). The mixture was pressed at 140 MPa into pellets, 6mm x 6mm (diam x height). Subsequently, these pellets were sintered in air at 1600 °C for 10 hours. During sintering the plasticizer was fully oxidized. After sintering the CeO_2 pellets were slightly red.

3.2. Characterization

All pellets/materials were characterizised before transfer into a capsule. Below follows a description of the different analysis:

- All materials are identified with X-ray diffraction analysis, which gives information about the crystal structure and the presence of impurities.
  The X-ray diffraction patterns were recorded with a Guinier-de Wolff camera using $K_{\alpha 1,2}$ radiation.
- The dimension and weight of each pellet were measured. The diameter was measured three times with a micrometer with a shift of 120° after each measurement. The height was measured twice at two different spots of the pellet. The weight was measured only once.
  From these results the densities were calculated.
- The porosity is measured with a mercury porosimeter.
- Of all materials pictures are made with a scanning electron microscope (SEM) with a magnitude of 500 and 1500. These pictures are made from embedded pollished pellets.

3.2.1. Spinel

- X-ray analysis shows a cubic spinel phase (PDF 21-1152) and a low concentration of an unidentified compound.
- Table 1 gives a list of dimensions of each spinel pellet. The mean density is 3.42 g/cm^3 corresponding to 95.6% theoretical density.
- With a mercury porosimeter it was not possible to measure any open porosity.
- Figure 2 shows SEM pictures with a magnitude of 500 and 1500 respectively. The holes in the spinel are apparently closed porosity.

3.2.2. YAG

- X-ray analysis shows a cubic phase (PDF 33-40).
- The dimensions and densities of each pellet are listed in Table 2. The mean density is 4.27 g/cm^3 which corresponds with 94% theoretical density.
- Similar to spinel, the YAG pellets appears to have no open porosity measured with mercury porosimetry.
- The SEM picture of the YAG pellets are displayed in figure 3.

3.2.3. Al_2O_3

- Al_2O_3 has a hexagonal crystal structure (PDF 43-1484).
- Table 3 gives a list of all dimensies and weights for the Al_2O_3 pellets. The mean density is 3.00 g/cm^3 with a theoretical density of 95%.
- Also Al_2O_3 has no open porosity.
- Figure 4 shows SEM pictures. The holes in the Al_2O_3 are closed porosity.

3.2.4. CeO_2

- CeO_2 has a cubic crystal structure (PDF 43-1002).
- Table 3 gives a list of all dimensies and weights for the CeO_2 pellets. The mean density is 3.00 g/cm^3 with a theoretical density of 80%.
- Also CeO_2 has no open porosity. This is somewhat strange when compared to the geometrical density of 80%. SEM pictures in figure 4 show large holes inside the cerium oxide. These holes are formed during sintering when the plasticizer is oxidized. The surrounding cerium oxide has no open porosity, so the large holes are completely insulated from the outer surface. Therefore no open porosity was measured despite of the large holes.
- Figure 5 shows SEM pictures. The cerium oxide contains large holes of about 100-150 µm and smaller holes of 2-5 µm.

4. CAPSULES

4.1. Capsule materials

For the present experiment three oxide materials were selected. These materials are most likely to be used in a LWR because of there relative stability towards water. For this reason we choosed zircaloy-4 as capsule material because it is commonly used in water cooled reactors.
The capsules were cut from a tube with an outside diameter of 10.76 mm and an inside diameter of 9.30 mm. The lenght of the capsule was about 100 mm. Figure 6 shows schematically the design of the capsules. The bottom and the cover were made from zircaloy-4 staff material and have a diameter of 9.0 mm and a thickness of 0.8 mm.

For CeO_2 we used another capsule material because there was no zircaloy-4 tube available with an outside diameter of ±6.3 mm. CeO_2, therefore, is being irradiated in a RVS 316L capsule. The design is similar to the zircaloy capsule. The outside diameter is 6.31 mm and the inside diameter is 5.33 mm. The length is also 100 mm.

On top of the pellets inside the capsules a spring was placed to fix the pellets. These springs were all made from RVS 304.

4.2. Loading and welding

Before loading of the capsules the bottom was welded in air. The welding was done by laser welding. On top of each pellet the pellet number was written with a pencil. Then the pellets were loaded with the smallest number at the bottom. Table 5 shows the loading scheme.
After the spring and cover were placed the capsule was transferred to a specially designed exsiccator [4]. The top of the exsiccator was made of planparallel quartz through which the laser welding technique could be applied. Before welding, the exsiccator was evacuated and filled with helium. During welding the exsiccator was flushed with helium gas to remove soot and control pressure and temperature inside the exsiccator.
The welding was done in two stages, first inside the exsiccator under a controlled helium atmosphere the capsule was gastight welded at low power. After this the capsules were taken out of the exsiccator and thoroughly welded at high power.
All weldings were checked by putting the capsule first in liquid nitrogen and subsequently in ethanol. None of the weldings showed any leaks.

4.3. Characterization

At the ECN Hot Cell Laboratory (LSO) the diameter of each capsule was measured at 0°, 120° and 240° with 1 mm intervals (Figure 7-13) and from each capsule a X-ray picture was made (Figure 14).

Conclusions

It has been possible to manufacture Spinel, YAG, Al_2O_3 and CeO_2 targets for the EFTTRA-T2 (RAS-2) irradiation programme. The density of all targets was about 95% theoretical density, only the cerium oxide targets were of a density of 83%. This was caused by the large grain size of the cerium oxide powder.

The CeO_2 and the Spinel pellets were manufactured directly by sintering of the green bodies while the Al_2O_3 and the Spinel pellets were mechanically processed to the right diameter after sintering of iso-statically pressed rods. The latter method gives a uniform pellet diameter, but in view of the fact that follow-up irradiations in the HFR will include samples containing UO_2, 20% enriched ^{235}U, it cannot be used for the production of the pellets of EFTTRA-T3. Therefore the direct sintering of green bodies will be investigated for Spinel.

After characterization of the pellets they were loaded into the capsules. The capsules were welded in a helium atmosphere by laser welding using an air-tight exsiccator. This methode previously applied to the EFTTRA-T1 iodine capsules, has been adapted to process safely capsules of various diameters and materials, including capsules filled with pellets containing enriched UO_2.

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TABLES

	diameter (mm)			height (mm)		weight (g)	Density (g/cm^3)	TD (%)
pil	1	2	3	1	2			
20	9,017	9,020	9,024	5,022	5,033	1,10739	3,447	96,3
21	9,061	9,072	9,061	4,759	4,748	1,05451	3,438	96,0
22	9,033	9,058	9,038	4,899	4,941	1,08533	3,435	95,9
23	9,040	9,049	9,039	4,917	4,903	1,07339	3,404	95,1
24	9,021	9,026	9,020	5,010	5,010	1,10530	3,451	96,4
25	9,069	9,083	9,078	4,762	4,843	1,06075	3,414	95,3
26	9,037	9,027	9,026	4,813	4,844	1,06439	3,442	96,1
27	9,030	9,024	9,030	5,021	5,014	1,09317	3,404	95,1
28	9,033	9,018	9,033	4,960	4,964	1,09113	3,435	96,0
29	9,039	9,022	9,031	4,998	4,993	1,10093	3,441	96,1
60	9,037	9,042	9,049	5,005	4,972	1,10056	3,435	96,0
61	9,088	9,125	9,078	4,835	4,863	1,06820	3,389	94,7
62	9,017	9,040	9,031	5,062	4,980	1,09790	3,415	95,4
63	9,035	9,046	9,038	4,983	4,970	1,07528	3,367	94,0
64	9,053	9,028	9,053	5,018	5,013	1,10697	3,435	96,0
65	9,021	9,025	9,021	4,955	4,970	1,09618	3,455	96,5
66	9,068	9,061	9,037	4,845	4,855	1,06757	3,418	95,5
67	9,061	9,059	9,053	4,824	4,826	1,07165	3,447	96,3
68	9,042	9,068	9,037	4,886	4,948	1,07942	3,413	95,3
69	9,060	9,063	9,073	5,000	4,951	1,08503	3,379	94,4

Table 1. Dimensions of Spinel pellets.
Pellets 20-29 are irradiated in capsule 2-2 and pellets 60-69 were irradiated in capsule 2-6.

	diameter (mm)			height (mm)		weight (g)	Density (g/cm3)	TD (%)
pil	1	2	3	1	2			
30	8,947	8,950	8,947	10,245	10,188	2,74102	4,266	93,7
31	9,005	8,998	8,999	10,214	10,199	2,77143	4,268	93,7
32	8,952	8,953	8,949	10,192	10,163	2,73833	4,275	93,9
33	8,961	8,961	8,963	10,302	10,280	2,76139	4,254	93,4
34	8,995	8,996	8,995	10,246	10,238	2,78829	4,284	94,1
70	9,009	9,007	9,007	10,208	10,182	2,77494	4,271	93,8
71	8,953	8,952	8,954	10,245	10,188	2,74250	4,264	93,7
72	8,984	8,984	8,992	10,136	10,151	2,75803	4,287	94,2
73	8,995	8,990	8,994	10,245	10,195	2,77084	4,268	93,7
74	8,953	8,950	8,952	10,131	10,142	2,72030	4,264	93,7

Table 2. Dimensions YAG pellets.

The pellets 30-34 and 70-74 were irradiated in the capsules 2-3 and 2-7 respectively.

pil	diameter (mm)			height (mm)		weight (g)	Density (g/cm³)	TD (%)
	1	2	3	1	2			
40	9,077	9,074	9,075	9,977	9,977	2,47067	3,828	96,4
41	9,064	9,069	9,070	9,939	9,938	2,46405	3,839	96,7
42	9,084	9,104	9,092	10,033	10,032	2,49045	3,822	96,3
43	9,085	9,091	9,086	9,941	9,948	2,47027	3,830	96,5
44	9,089	9,085	9,086	9,971	9,971	2,47980	3,835	96,6
80	9,103	9,097	9,096	9,977	9,977	2,48144	3,825	96,4
81	9,100	9,058	9,044	9,951	9,949	2,45610	3,823	96,3
82	9,089	9,092	9,096	9,876	9,876	2,45076	3,822	96,3
83	9,089	9,084	9,093	9,982	9,983	2,47427	3,820	96,2
84	9,079	9,067	9,091	10,009	10,009	2,47394	3,818	96,2

Table 3. Dimensions Al_2O_3 pellets.

The pellets 40-44 and 80-84 were irradiated in the capsules 2-4 and 2-8 respectivily.

pil	diameter (mm)			height (mm)		weight (g)	Density (g/cm^3)	TD (%)
	1	2	3	1	2			
1	5,138	5,121	5,121	5,350	5,350	0,66338	6,007	83,2
2	5,188	5,182	5,178	5,231	5,230	0,67710	6,136	85,0
3	5,125	5,139	5,156	5,806	5,804	0,70465	5,850	81,0
4	5,132	5,135	5,096	5,508	5,508	0,66499	5,862	81,2
5	5,110	5,106	5,111	5,531	5,530	0,68547	6,046	83,7
6	5,198	5,190	5,153	5,731	5,729	0,72229	5,981	82,8
7	5,183	5,178	5,188	5,950	5,948	0,75495	6,015	83,3
8	5,145	5,149	5,116	5,386	5,384	0,65986	5,913	81,9
9	5,187	5,181	5,191	5,313	5,313	0,68553	6,108	84,6

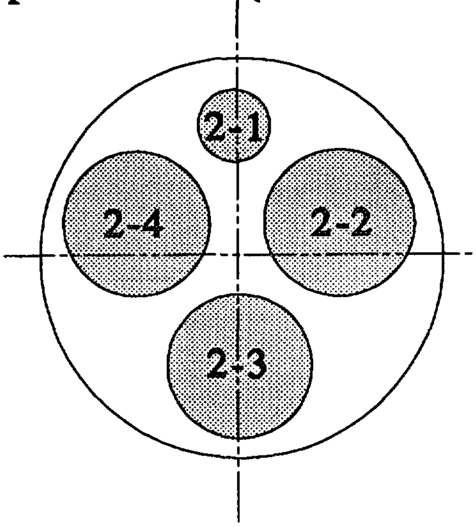
Table 4. Dimensions CeO_2 pellets.

Capsule n°	Sample holder n°	Target material	Target length (mm)	Target diameter (mm)	Capsule material	Spring material
2-2	2	Spinel	50	9	Zircaloy-4	RVS 304
2-3	2	YAG	50	9	Zircaloy-4	RVS 304
2-4	2	Al_2O_3	50	9	Zircaloy-4	RVS 304
2-5	2.1	CeO_2	50	5	RVS 316L	RVS 304
2-6	2.1	Spinel	50	9	Zircaloy-4	RVS 304
2-7	2.1	YAG	50	9	Zircaloy-4	RVS 304
2-8	2.1	Al_2O_3	50	9	Zircaloy-4	RVS 304

Table 5. Loading scheme RAS-2 capsules.

FIGURES

Sample holder 2 (EFTTRA-T2)



Sample holder 2.1 (EFTTRA-T2bis)

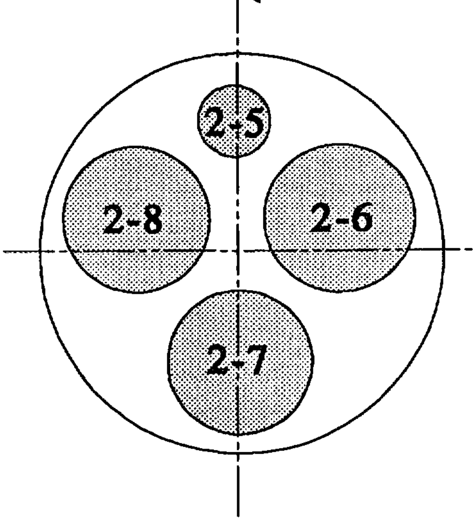


Figure 1. Schematic view of the cross section of the EFTTRA-T2 and EFTTRA-T2bis sample holders loaded with the capsules 2-1 to 2-8. Capsules 2-2 to 2-8 are filled with the inert matrices (see table 5).

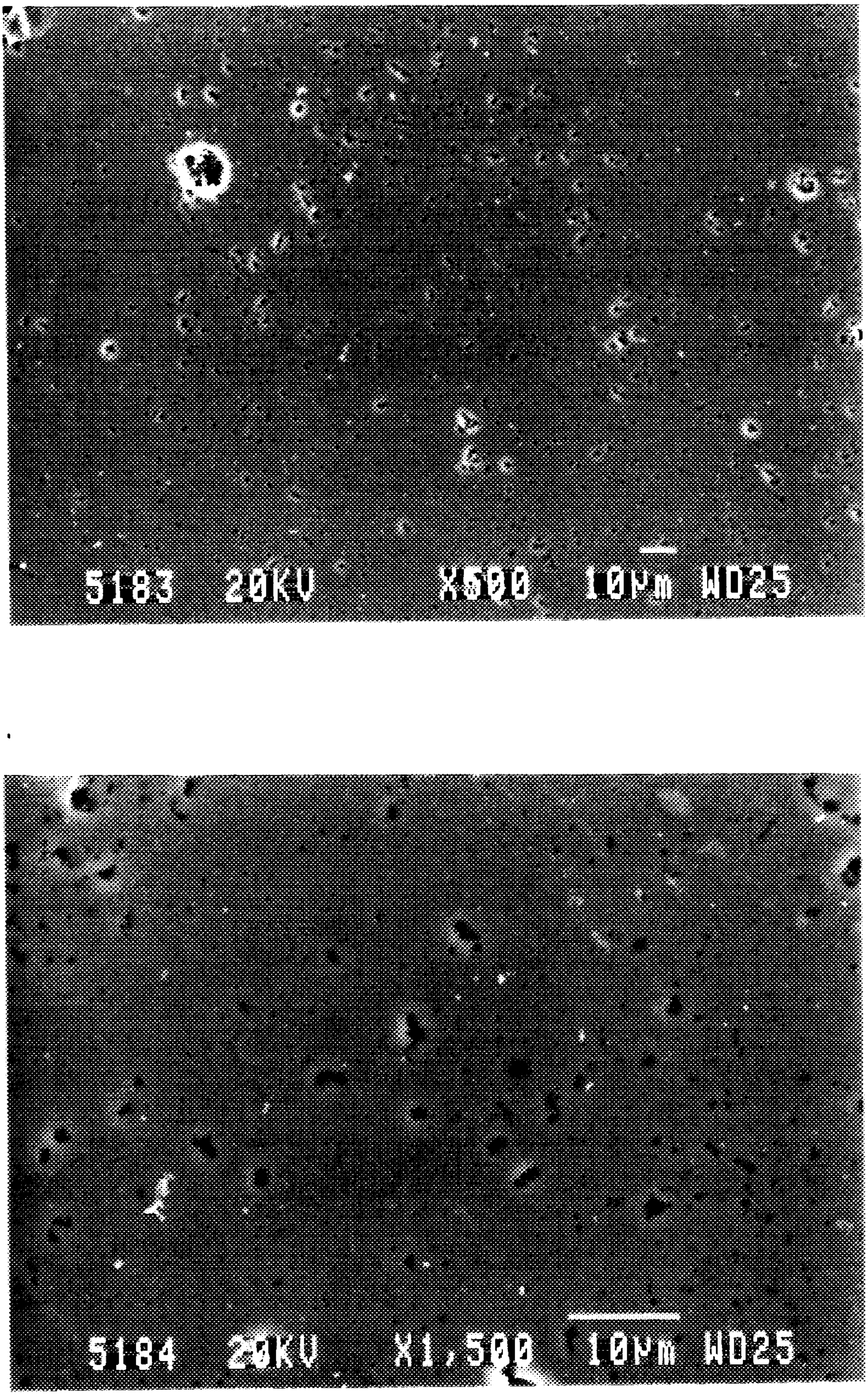


Figure 2. Scanning Electron Microscope picture of spinel.
Top: 500 x Bottom: 1500 X

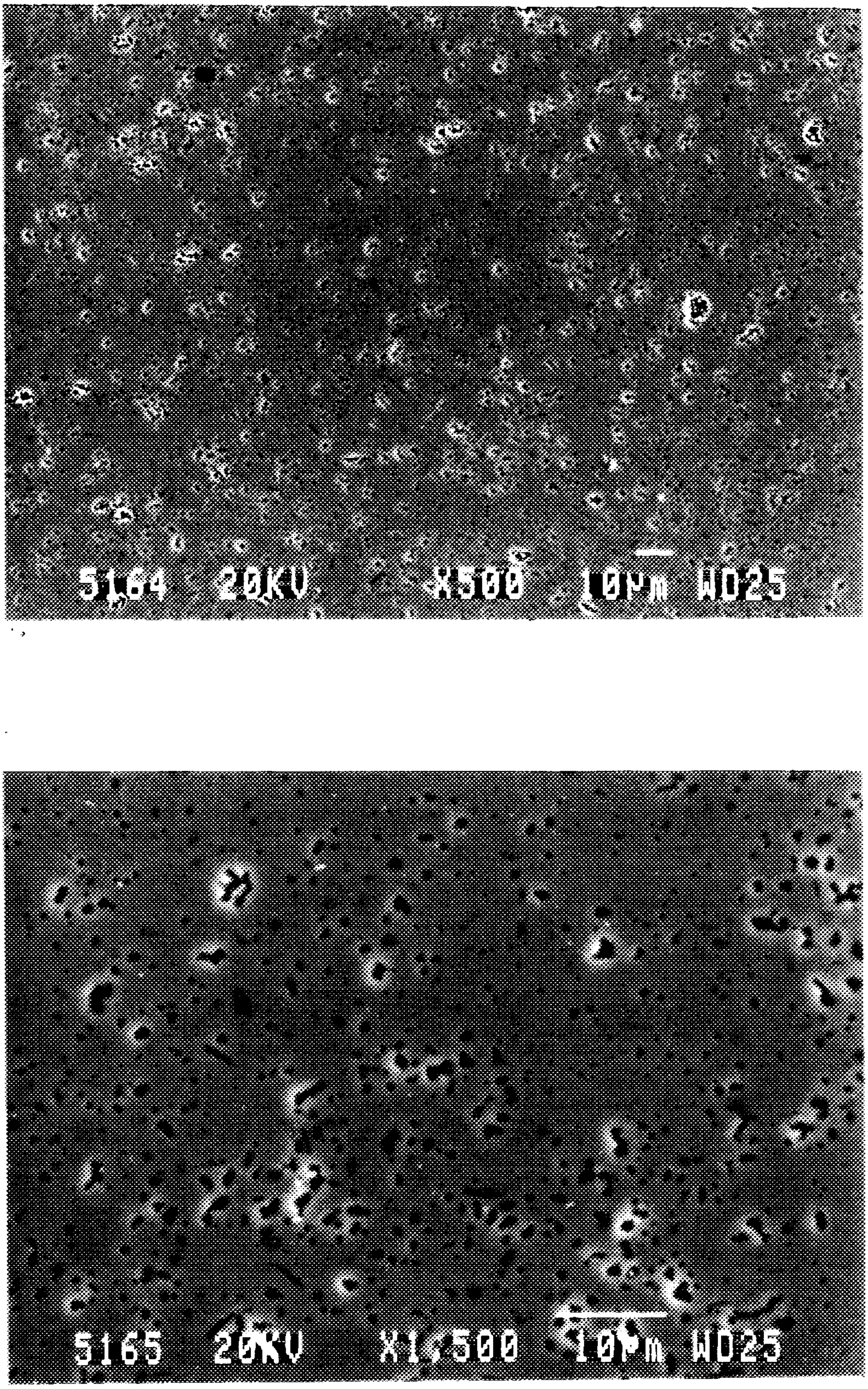


Figure 3. Scanning Electron Microscope picture of YAG.
Top: 500 x Bottom: 1500 X

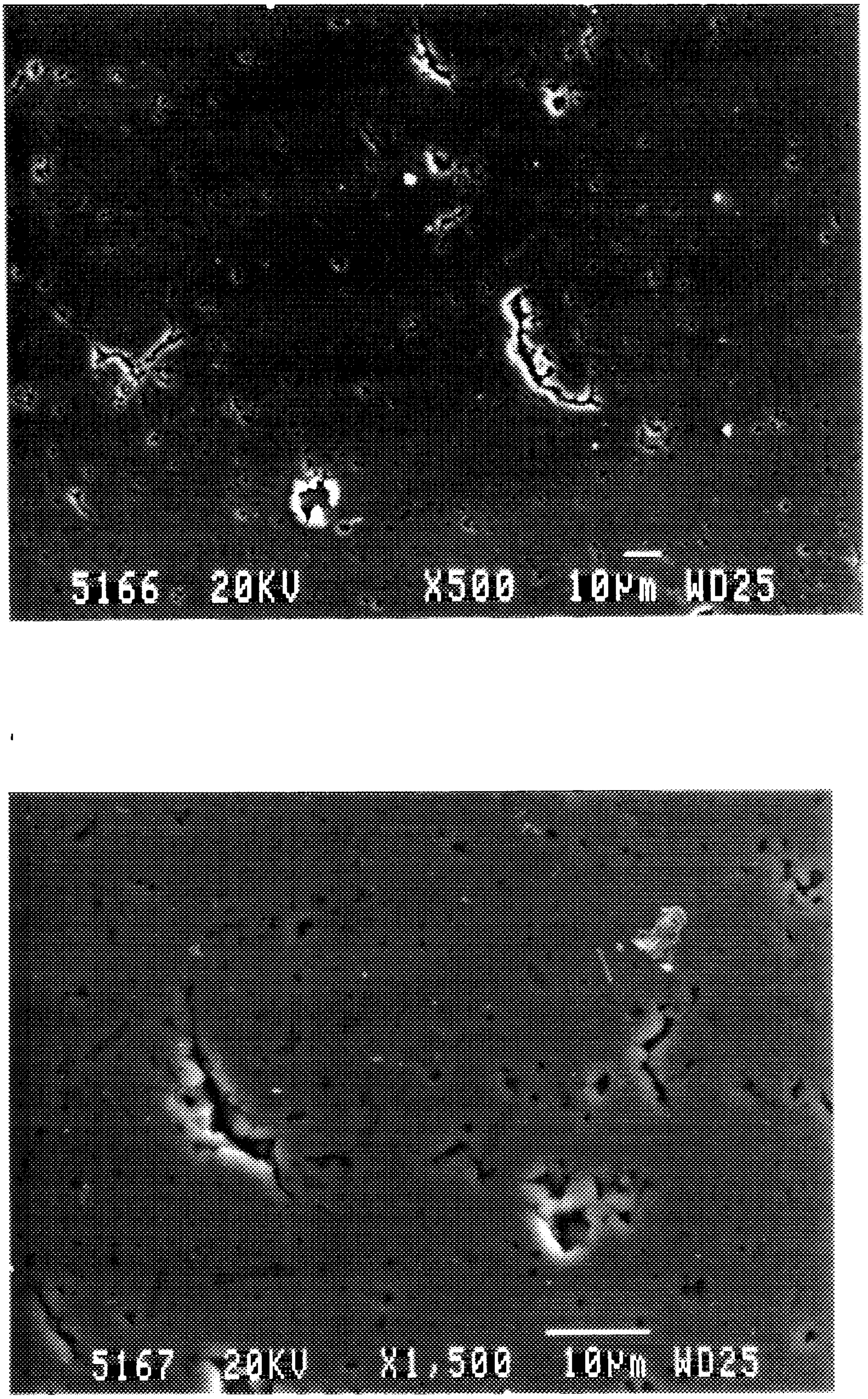
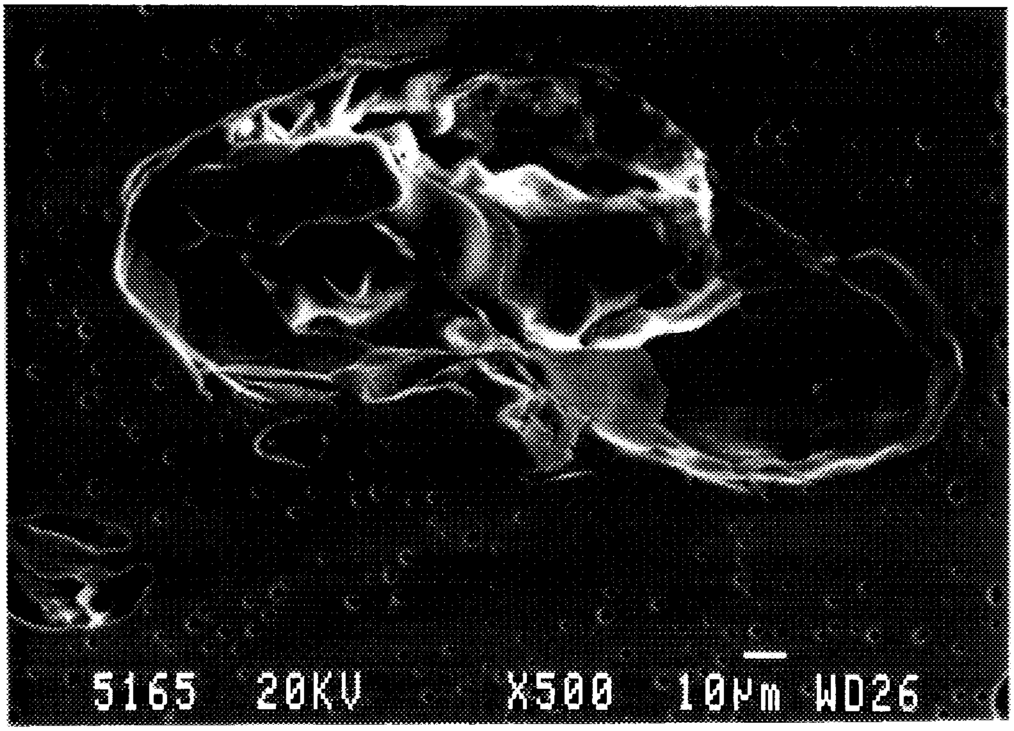


Figure 4. Scanning Electron Microscope picture of Al_2O_3.
Top: 500 x Bottom: 1500 X



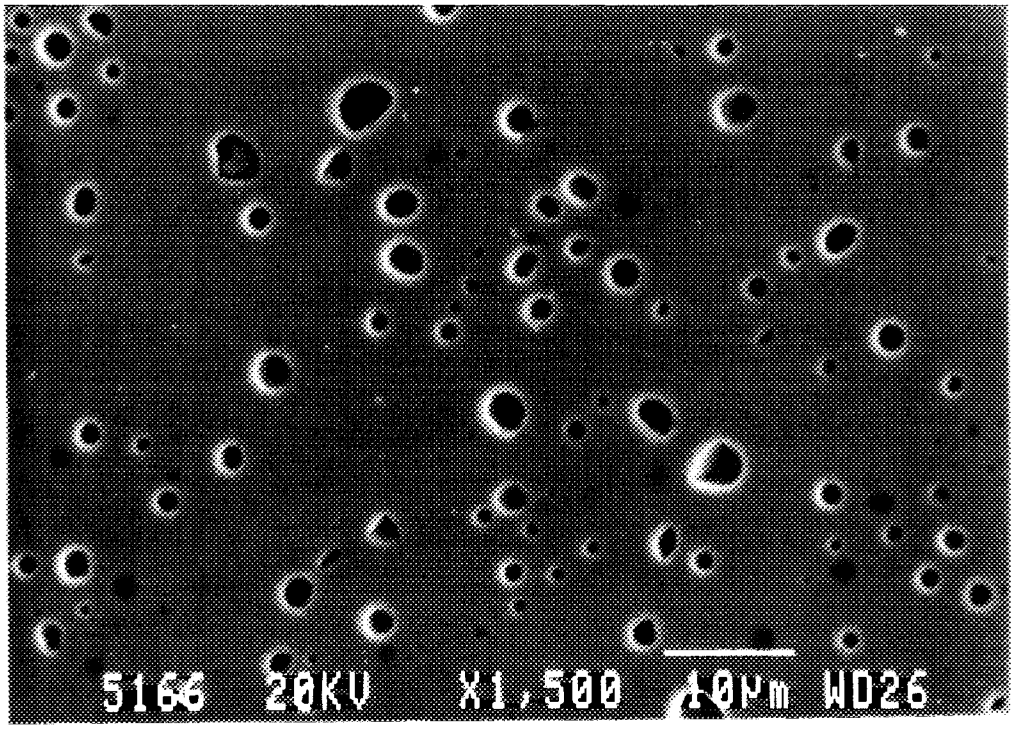


Figure 5. Scanning Electron Microscope picture of CeO_2.
Top: 500 x Bottom: 1500 X

7 april 1995

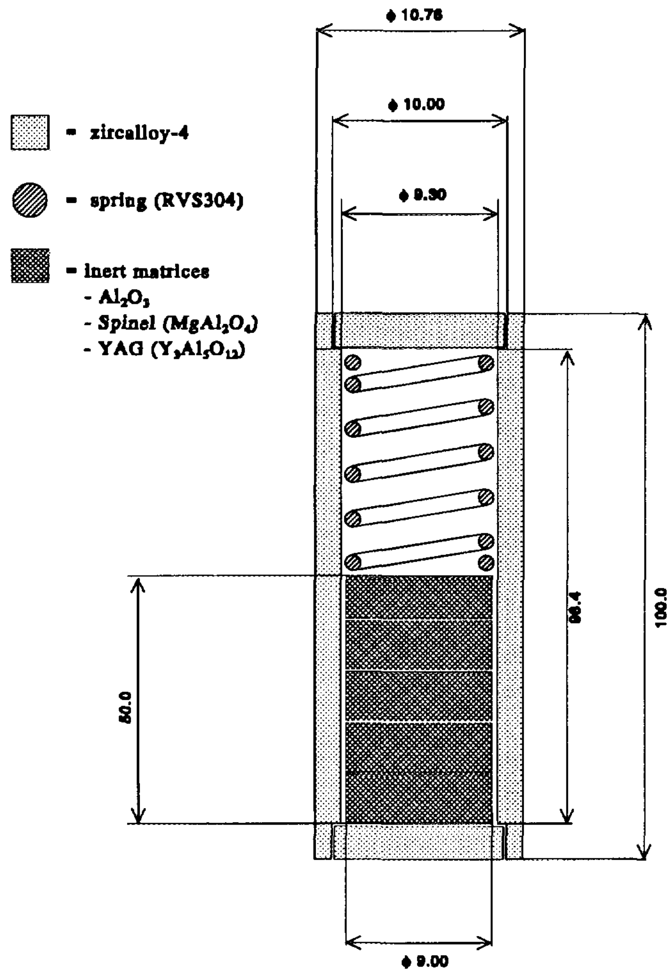


Figure 6. The zircaloy capsule for irradiation of Al_2O_3, spinel and YAG. (All dimensions in millimeters).

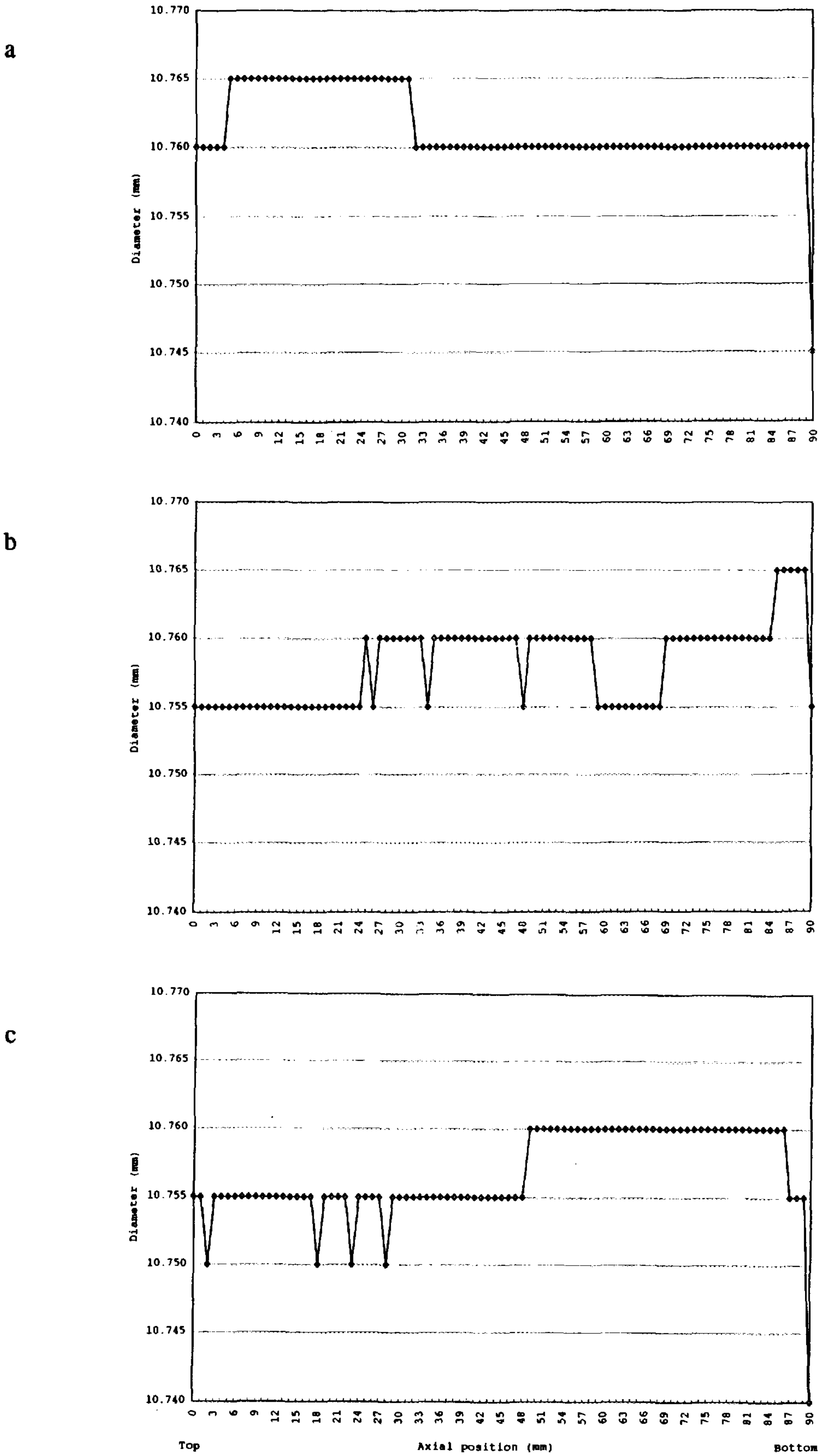


Figure 7 a,b,c. Diameter of capsule RAS 2-2 as a function of the axial position at radial positions of respectively 0°, 120° and 240°.

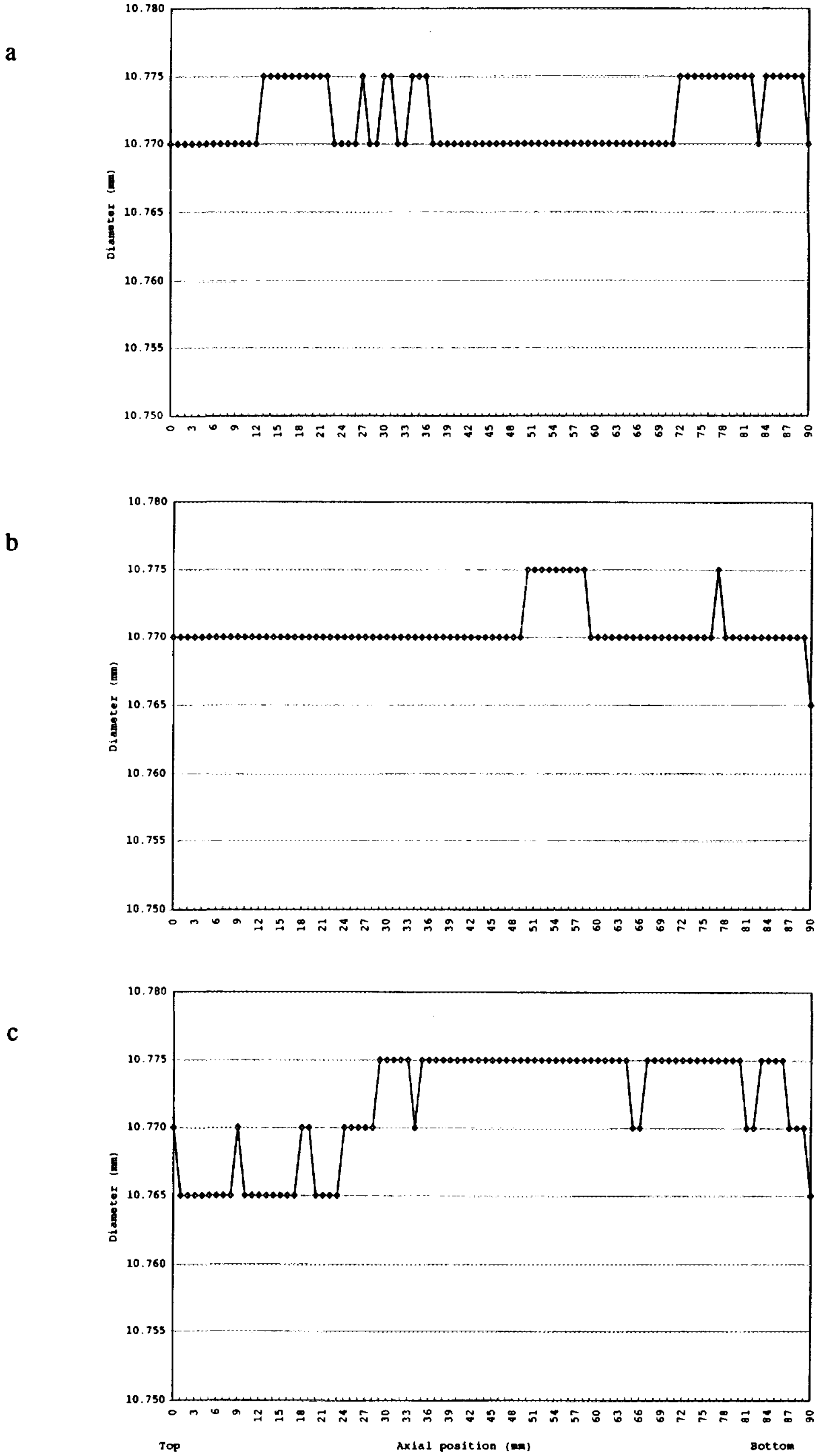


Figure 8 a,b,c. Diameter of capsule RAS 2-3 as a function of the axial position at radial positions of respectively 0°, 120° and 240°.

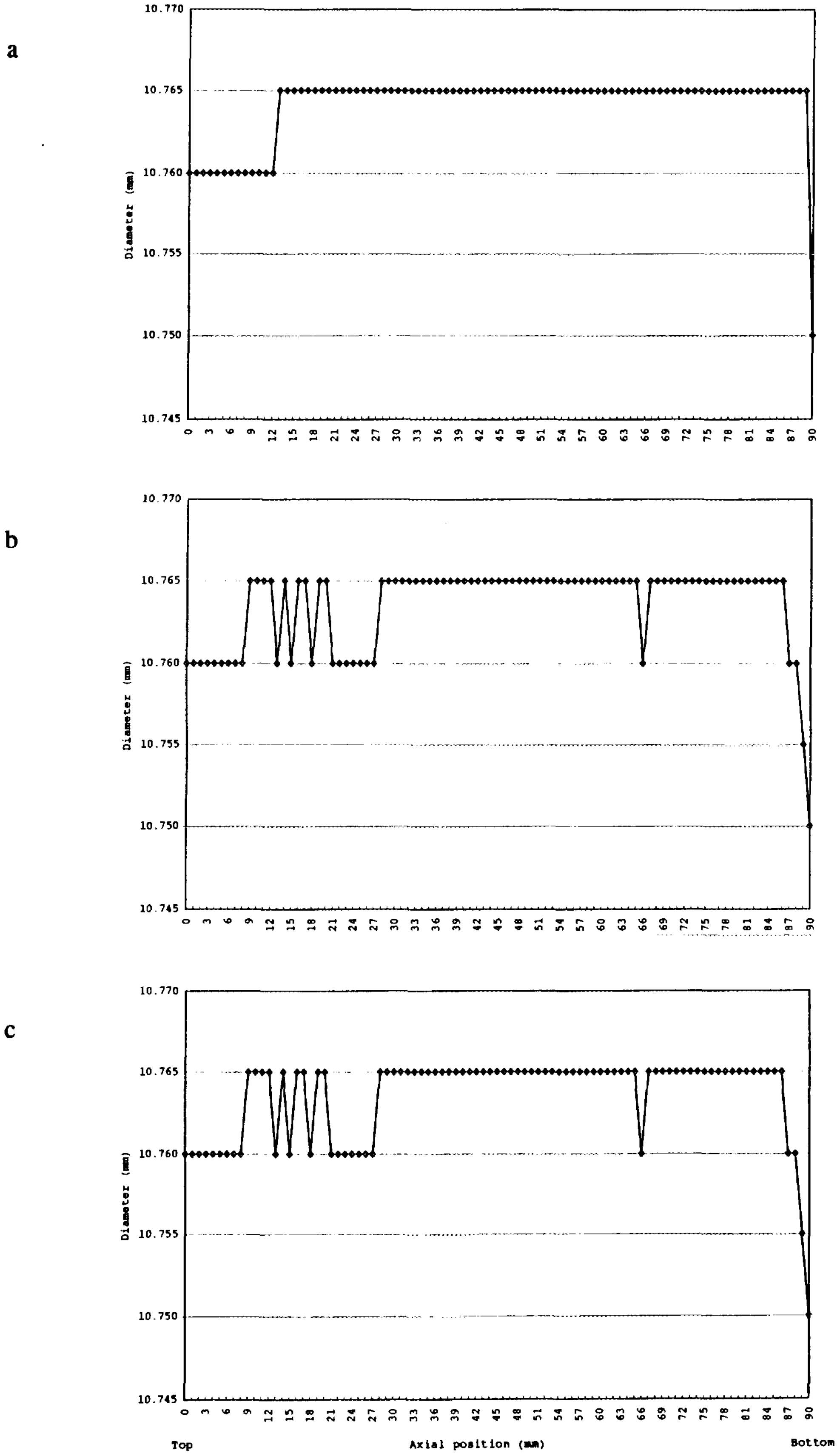


Figure 9 a,b,c. Diameter of capsule RAS 2-4 as a function of the axial position at radial positions of respectively 0°, 120° and 240°.

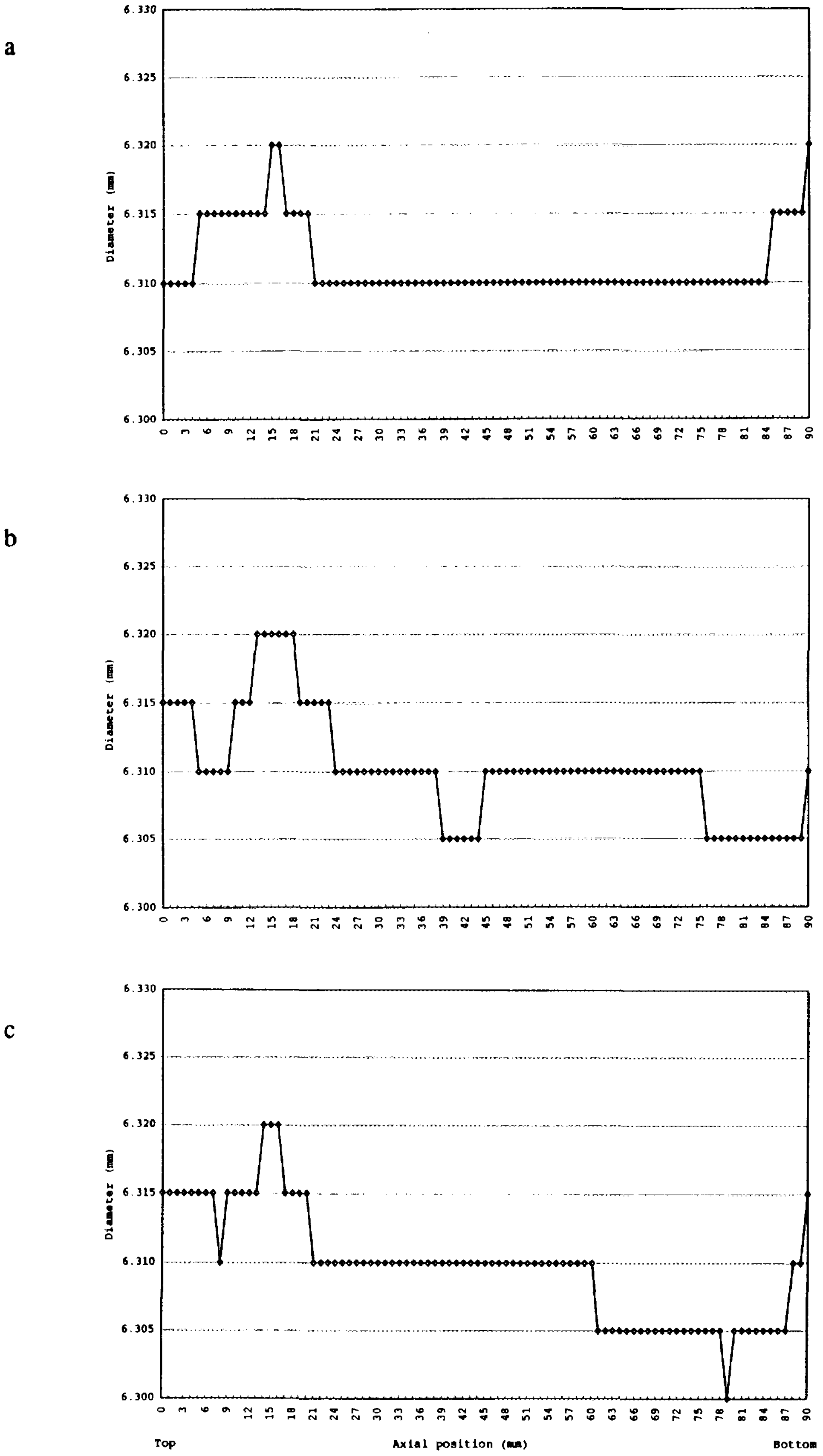


Figure 10 a,b,c. Diameter of capsule RAS 2-5 as a function of the axial position at radial positions of respectively 0°, 120° and 240°.

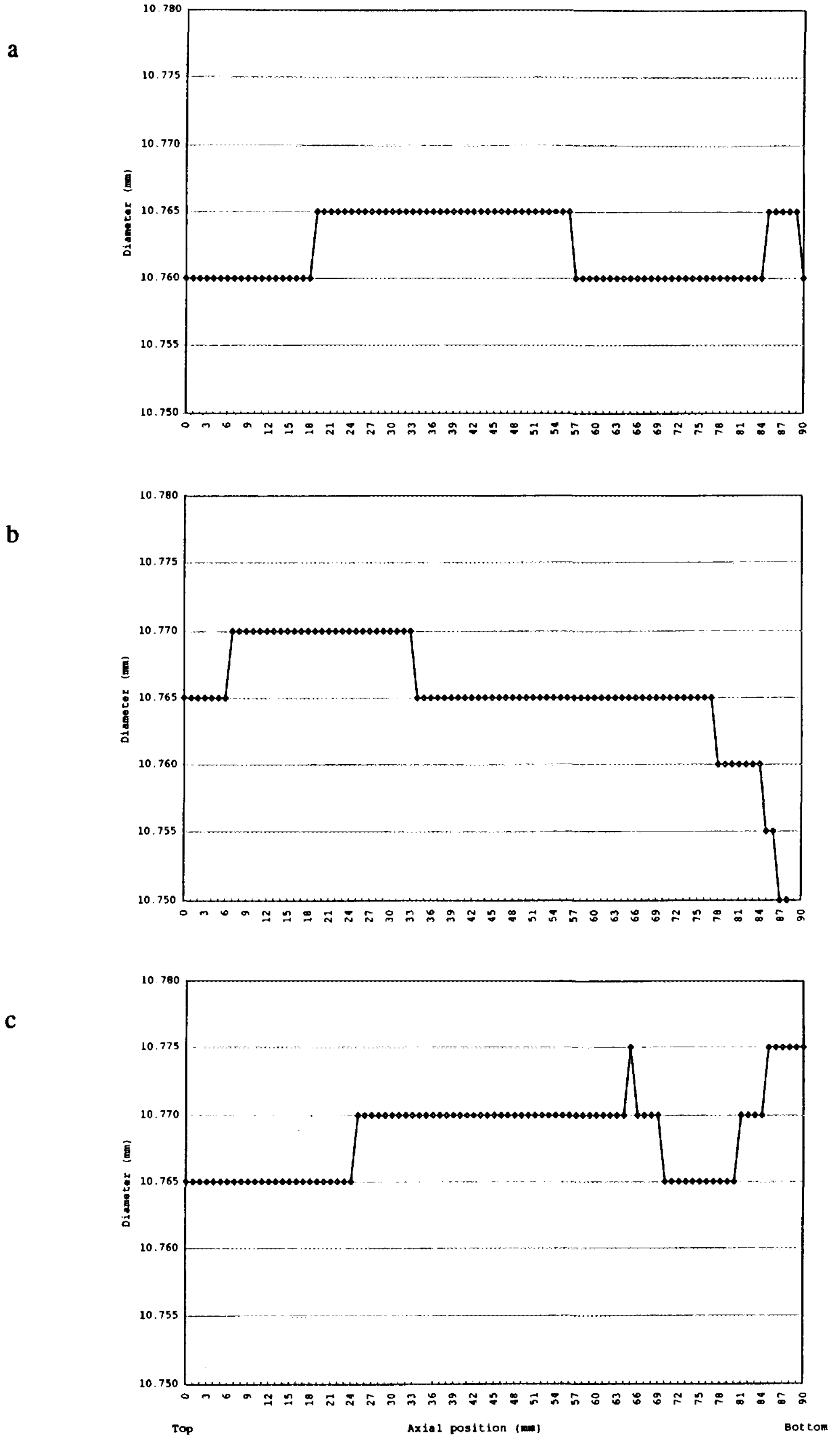


Figure 11 a,b,c. Diameter of capsule RAS 2-6 as a function of the axial position at radial positions of respectively 0°, 120° and 240°.

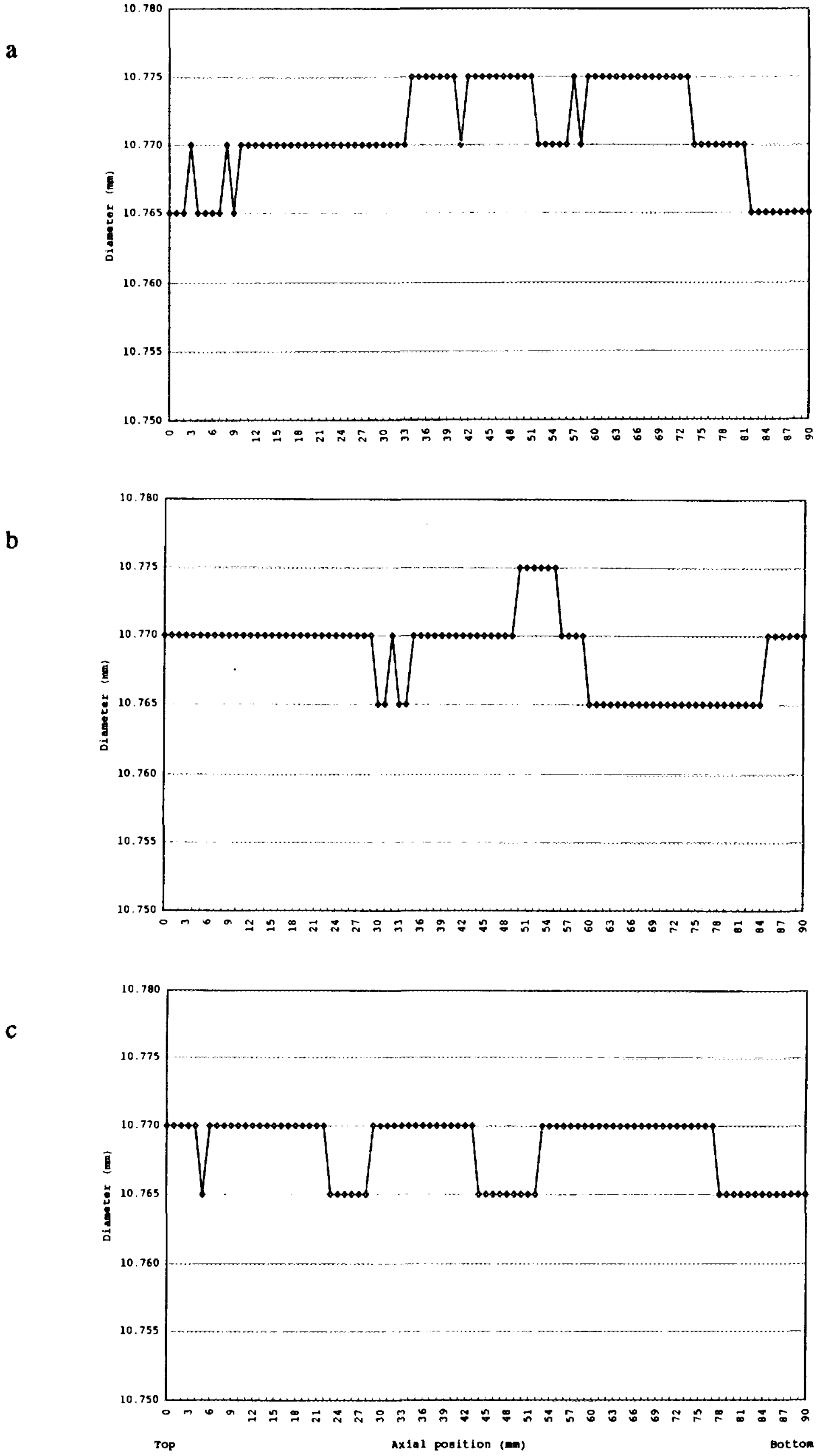


Figure 12 a,b,c. Diameter of capsule RAS 2-7 as a function of the axial position at radial positions of respectively 0°, 120° and 240°.

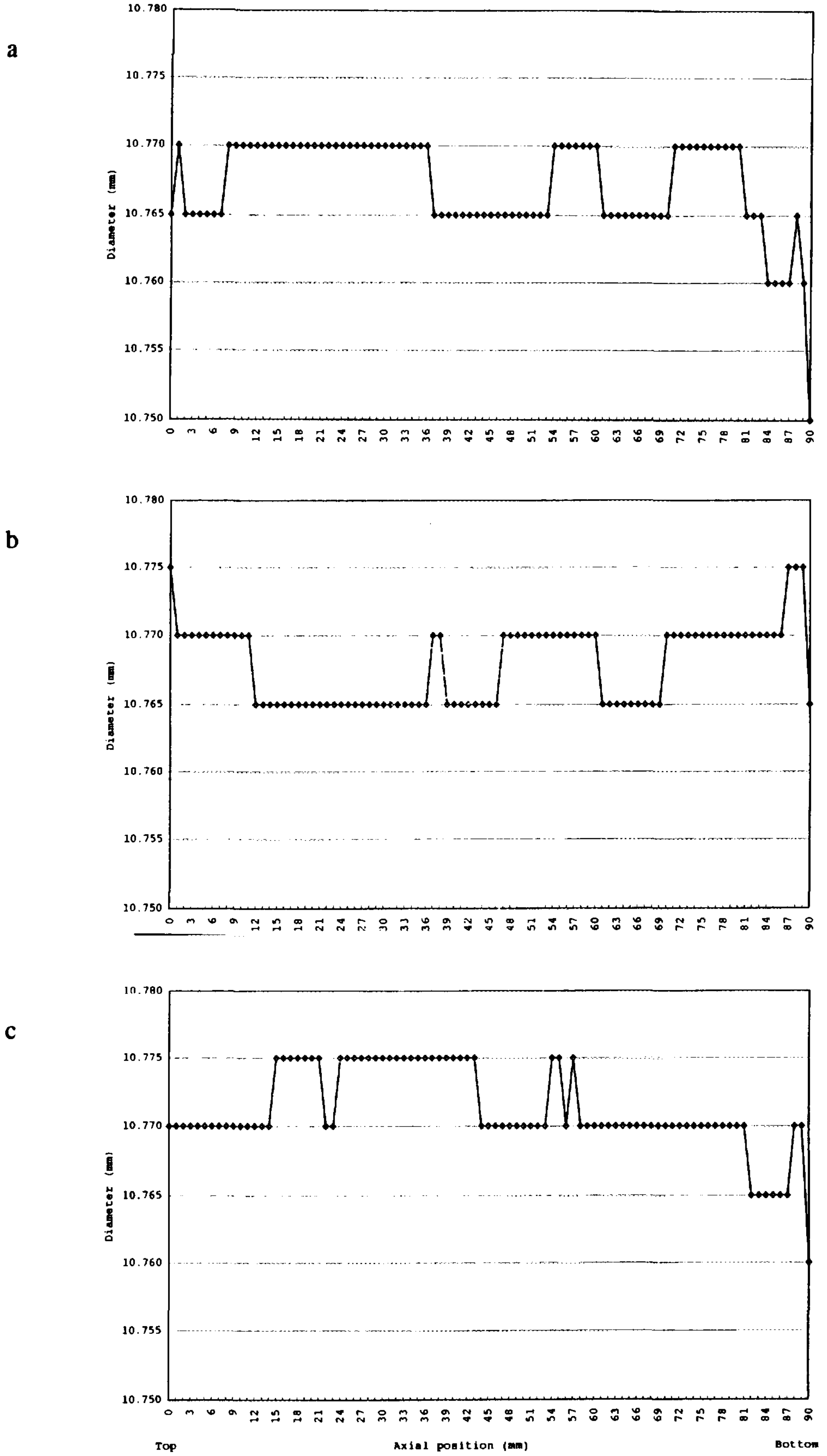


Figure 13 a,b,c. Diameter of capsule RAS 2-8 as a function of the axial position at radial positions of respectively 0°, 120° and 240°.

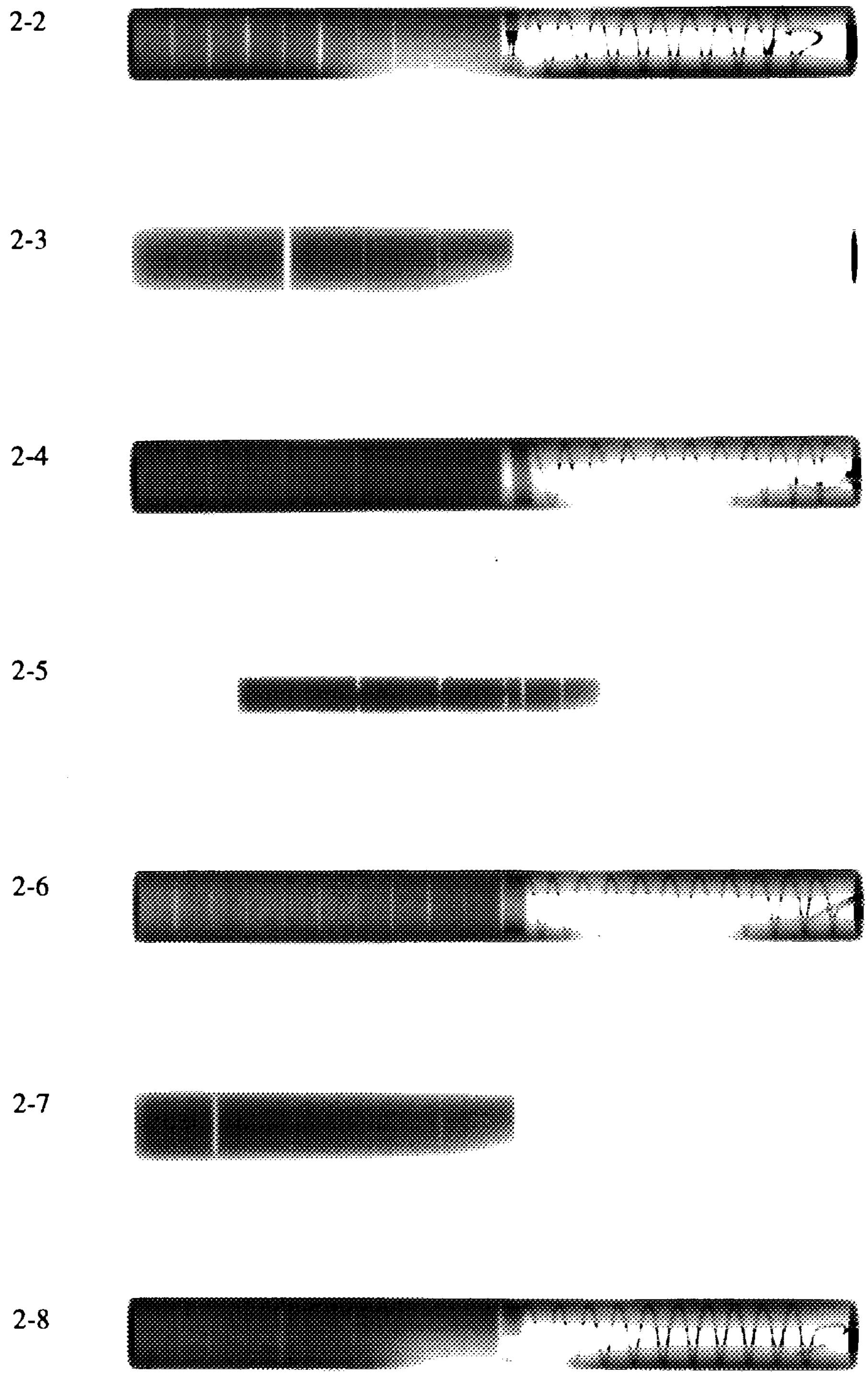


Figure 14. X-ray pictures of capsules 2-2 to 2-8. Capsules 2-2 and 2-6 are each filled with 10 spinel pellets. Capsules 2-3 and 2-7 are each filled with 5 YAG pellets. Capsules 2-4 and 2-8 are each filled with 5 Al_2O_3 pellets and capsule 2-5 contains 9 CeO_2 pellets. Notice that the 7th pellet is broken. All pellets are fixed at their position with a stainless steel spring.