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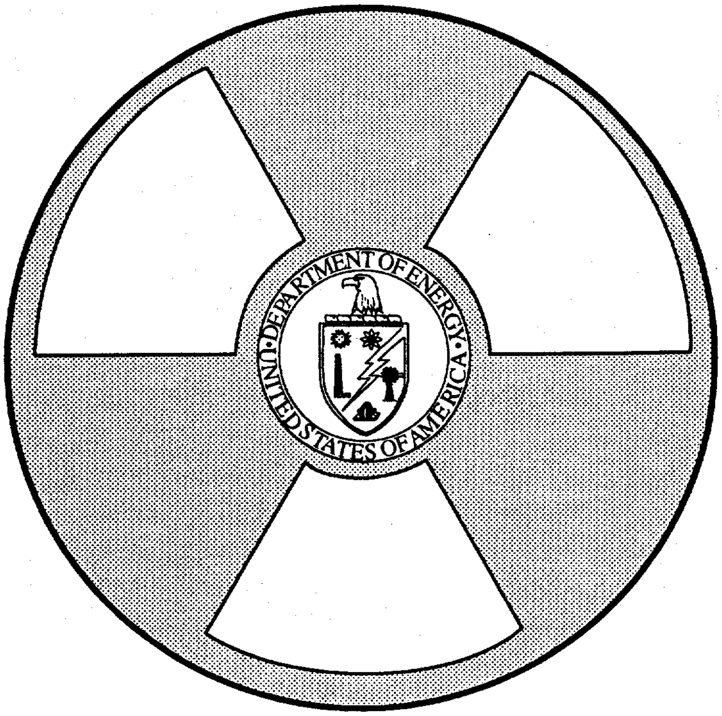

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DISSOLUTION RATE AND RADIATION DOSIMETRY OF METAL TRITIDES

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Abstract

Metal tritides including titanium tritide (Ti ^3H_x) and erbium tritide (Er ^3H_x) have been used as components of neutron generators. These compounds can be released to the air as aerosols during fabrication, assembling, and testing of components or in accidental or fugitive releases; as a result, workers may be exposed to these compounds by inhalation. A joint research project between Sandia National Laboratories and the Inhalation Toxicology Research Institute was initiated last fall to investigate the solubility of metal tritide particles, to determine retention and translocation of inhaled particles in animals, and to develop an internal dosimetry model. The current understanding of metal tritides and their radiation dosimetry for internal exposure is very limited. The ICRP Report 30 does not provide for tritium dosimetry in metal tritide form. However, a few papers in the literature suggest that the solubility of metal tritide could be low. The current radiation protection guidelines for metal tritide particles are based on the assumption that the biological behavior is similar to tritiated water which could be easily absorbed into body fluid, and therefore, a relatively short biological half life (10 days). If the solubility is low, the biological half life of metal tritide particles and the dosimetry of inhalation exposure to these particles could be quite different from tritiated water. This would have significant implications in the current health protection guidelines including annual limits of intakes and derived air concentrations. The preliminary results of our metal tritide dissolution study indicated that the solubility of titanium tritide is low.

Introduction

Metal tritides including titanium tritide (Ti ^3H_x) and erbium tritide (Er ^3H_x) have been used as components of neutron generators. These compounds can be released to the air as aerosols during fabrication, assembling, and testing of components or in accidental or fugitive releases; as a result, workers may be exposed to these compounds by inhalation. The current health protection guidelines for metal tritide particles are based on the assumption that the biological behavior of these components is similar to tritiated water (HTO). In the ICRP Report No. 30, HTO is classified as very soluble in the body. It is distributed uniformly to all soft tissues following uptake, and its retention is described by a single exponential decay function in which the effective retention half-life is 10 days. Little information is available on the dissolution behavior of metal tritide particles in biological systems. However, studies of tritium leaching from titanium and zirconium tritides suggest that they are insoluble in aqueous solutions (Miller, 1982; Miller and Bokwa, 1985). Thus, the current health protection guidelines may not be appropriate for metal tritides.

The dissolution rate of particles deposited in the respiratory tract is a major factor governing retention and translocation of their constituents to other organs in the body. Radioactive particles that dissolve slowly in lung fluid tend to remain in the lung tissue for a long period of time, and the biological effects of the particles are usually confined to the region near the deposition site (i.e. the lung tissue). On the other hand, highly soluble materials, such as HTO, that deposit in the respiratory tract will be translocated to other organs and body fluid more readily and may therefore have a shorter retention time in the body.

Dissolution rates of radioactive particles have been measured by immersing the particles in various aqueous solutions and by determining the amount of dissolved radionuclides in the solution. This technique provides a simple, cost-effective method to estimate dissolution rates for respirable, radioactive particles. It is often used as a screening method to classify materials according their solubilities and is sometimes used in dosimetric models if *in vivo* dissolution data are not available.

The purpose of this study was to investigate the dissolution behavior of both titanium and erbium tritide particles in simulated biological fluids and in rats. Data from these studies will provide information to estimate the dosimetry of inhaled metal tritides. The dosimetric model can then be used as the technical basis for setting health protection limits, including the annual limit on intake and the derived air concentration for DOE facilities.

Experimental Methods

The radioactive metal tritides including titanium and erbium tritide were obtained from the Matin Marietta Pinellas Plant, Largo, FL. These materials have been components of neutron generators and were ground into powders. Samples of the powders were examined in an optical microscope, and particle size was determined using an image analyzer.

Serum ultrafiltrate (SUF), which consists of various salts as listed in Table 1 (Eidson and Griffith, 1984), was used to determine the dissolution rates of metal tritides. A static dissolution system as described by Kanapilly (1979) was used in the study. About 10 mg of powder were used for each sample. The particles were sandwiched between two 47-mm membrane filters (Tuffryn HT-100, 0.2 μm pore size, Millipore Corp., Bedford, MA) and secured in a Teflon filter holder (Free Flow Filter Holder 04-112, In Tox Products, Albuquerque, NM). Duplicate samples were tested. The filter holders were placed individually into 500 mL glass flasks containing 100 mL of SUF incubated in a 37°C water bath.

The *in vitro* dissolution apparatus was designed to measure the tritium in the gas phase and in solution. In most dissolution experiments, only the radionuclides dissolved in the solution were measured. However, the dissolved tritium in metal tritides could exist in the gas phase or could be exchanged into HTO (Miller and

Bokwa, 1985). Both species were accounted for in our *in vitro* experiment. Figure 1 shows the schematic diagram of the dissolution system consisting of a water bath, dissolution flasks, catalyst columns, propylene glycol traps, and temperature controllers. The catalyst columns (Sheen *et al.*, 1975; Jabert and Murphy, 1988) were used to convert tritium gas released from the powder into HT, which was subsequently trapped in propylene glycol bubblers. The catalyst column was packed with a precious metal sponge catalyst (GPT, Inc., Manalapan, NJ). The column was located inside a tube furnace maintained at 550 °C. The conversion efficiency of the catalyst column was determined using HT generated by reacting magnesium metal with HTO water (Amershan International, Amershan, UK) and sulfuric acid (0.1 M). The HT passed through two columns in series, and the amounts of HT collected were counted. The dissolution kettle was kept sealed during the dissolution study. One hour before the solution was changed, air (with 5% CO_2, Argyle Supply Co., Albuquerque, NM) was passed through the flask, carrying the released HT and water vapor into two propylene glycol traps (20 mL) to remove water and HTO vapors in the effluent. The HT then passed through a packed column of catalyst maintained at 550°C. The HT was oxidized by the catalyst into HTO. The HTO passed through two more propylene glycol traps. The collected HTO in propylene glycol bubblers and in solution in the flask were analyzed for ^3H using liquid scintillation counting methods (Packard Tri-Carb®, Model 2500TR, Packard Instrument Co., Meriden, CT). The flow rate through the system was 100 mL/min for 1 hour. Then new solution replaced the solution in the dissolution flask. Some of the HTO remained in the catalyst. Air containing 1% hydrogen (Argyle Supply Co., Albuquerque, NM) was used to purge the catalyst column for 3 to 4 hrs at a flow rate of 1.1 L/min to remove any HTO trapped in the catalyst column.

Solvents were changed at 1, 6, 24, 48 and 72 hours, then twice weekly for 29 days. After the last change of solution, the remaining particles in the filter holder were dissolved in adding 400 mL of 5M HCl. The titanium tritide material completely dissolved in 10 to 13 days. The tritiated water and tritium were collected and counted. The radioactivities recovered from the filter holder and those from previous changes were added to get the material balance. The percentage of ^3H dissolved from the particles was plotted as a function of time. From these curves, the dissolution half-times in the SUF were estimated.

Results

Figure 1 shows the particle size distribution of titanium tritide powder expressed as projected area diameter. The size distribution could be fitted with a lognormal distribution with the count median diameter of 103 μm and the geometric standard deviation of 1.58.

Table 2 shows the efficiency of the catalyst column for converting tritium gas into tritiated water. The first column converted over 90% of the gas with little collected in the second column. Therefore, only one column for each sample was used in the dissolution study with an assumed mean efficiency of 93.3%.

Figure 3 and 4 show the fraction dissolved per day as tritiated water and as tritium gas, respectively. The amount released as tritium gas was two orders of magnitude smaller than that released as tritiated water. Table 2 shows the material balance for the two samples used in the study. The amount dissolved in 29 days was only 5.1%. The specific activities for the two samples were 127 and 272 mCi/g, respectively, indicating that the samples might not be homogeneous.

Figure 5 shows the retention curve for the titanium tritide. The retention curve can be expressed as a single exponential decay curve (t in minutes):

$$R = \exp(-7.99\times10^{-5}t).$$

Thus, the retention or clearance half time was 362 days.

Discussion

We describe preliminary results for the *in vitro* dissolution rate of titanium tritide powder. Our results showed a slow dissolution rate with less than 0.5% dissolved per day. The majority of tritium was released as tritiated water. This result was similar to those reported by Miller and Bokwa (1985) using titanium tritide in a sponge form in aqueous solutions of salts. Our retention half time was 362 days. If this dissolution and clearance pattern is confirmed in the planned animal study, then the internal dosimetry of this material should be very different from tritiated water which has a biological half time in the body of 10 days. It will place metal tritide in the Y class material in terms of its dissolution classification instead of D class for tritiated water. We plan to continue the *in vitro* dissolution study of erbium tritide using the same solution and technique followed by a study in which rats will be injected metal tritide. These data will be used to develop an internal dosimetry model of metal tritide following inhalation exposure. The new model should be useful for health protection purposes.

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Table 1

Composition of Serum Ultrafiltrate

ACS Reagent Grade Chemicals	FW	mMoles/L	g/L	Amount needed for 10 L
NaCl	58.40	116	6.779	67.79 g
NH_4Cl	53.49	10	0.535	5.35 g
$NaHCO_3$	84.01	27	2.268	22.68 g
NaH_2PO_4 H_2O	137.99	1.2	0.116	1.66 g
Na_3 Citrate $2H_2O$	294.10	0.2	0.059	0.59 g
Glycine	75.07	5.0	0.375	3.75 g
L-Cysteine Hydrochloride	175.63	1.0	0.176	1.76 g
H_2SO_4 (conc.)	98.08	0.5	0.03 ml/L	0.3 ml
$CaCl_2$ $2H_2O$	146.92	0.2	0.029	0.29 g
DTPA[a]		0.2		
ABDCb[b]	----	50ppm	0.1 ml/L	1.0 ml

[a] DTPA, diethylenetriaminepentaacetic acid

[b] ABDC, alkylbenzyl-dimethyl-ammonium chlorides, 50% by volume.

Note: H_2O used for preparation of SUF will be deionized and distilled.

Table 2

Efficiency of Catalyst Column

	First Column	Second Column
Run 1	89.7 %	10.3 %
Run 2	95.4 %	4.6 %
Run 3	94.7 %	5.3 %
Mean	93.3 %	
SD	3.1 %	

Table 3

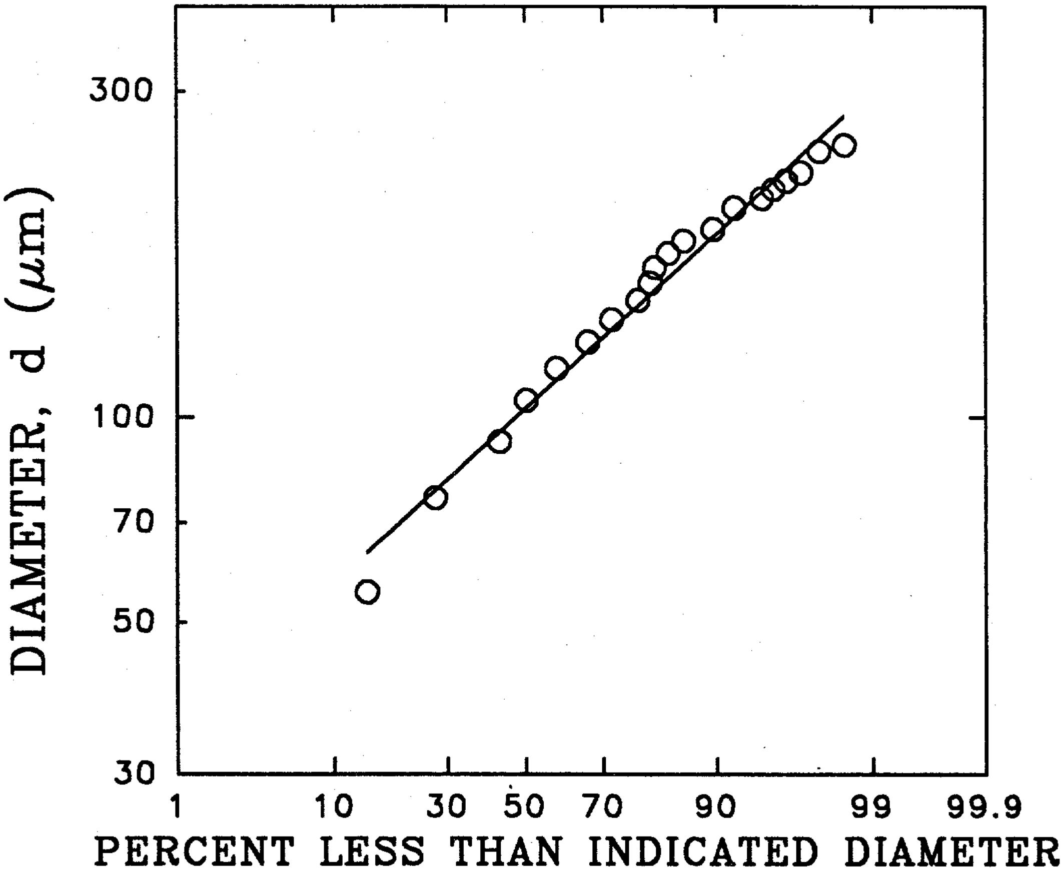
Material Balance and Specific Activity of Titanium Tritide

	Activity Dissolved in Solution µCi	Activity Evolved as Gas µCi	Total Activity of Sample µCi	Mass of Sample mg	Specific Activity mCi/g
Run 1	66	.37	1404	11.08	127
Run 2	158	.26	2898	10.64	272

Figure Legends

Figure 1	Particle size distribution of titanium tritide powder.
Figure 2	Schematic of the dissolution experiment apparatus.
Figure 3	Percent activity of tritium per day dissolved as tritiated water.
Figure 4	Percent activity of tritium per day evolved ad tritium gas.
Figure 5	Retention curve of titanium tritide powder in the solution.

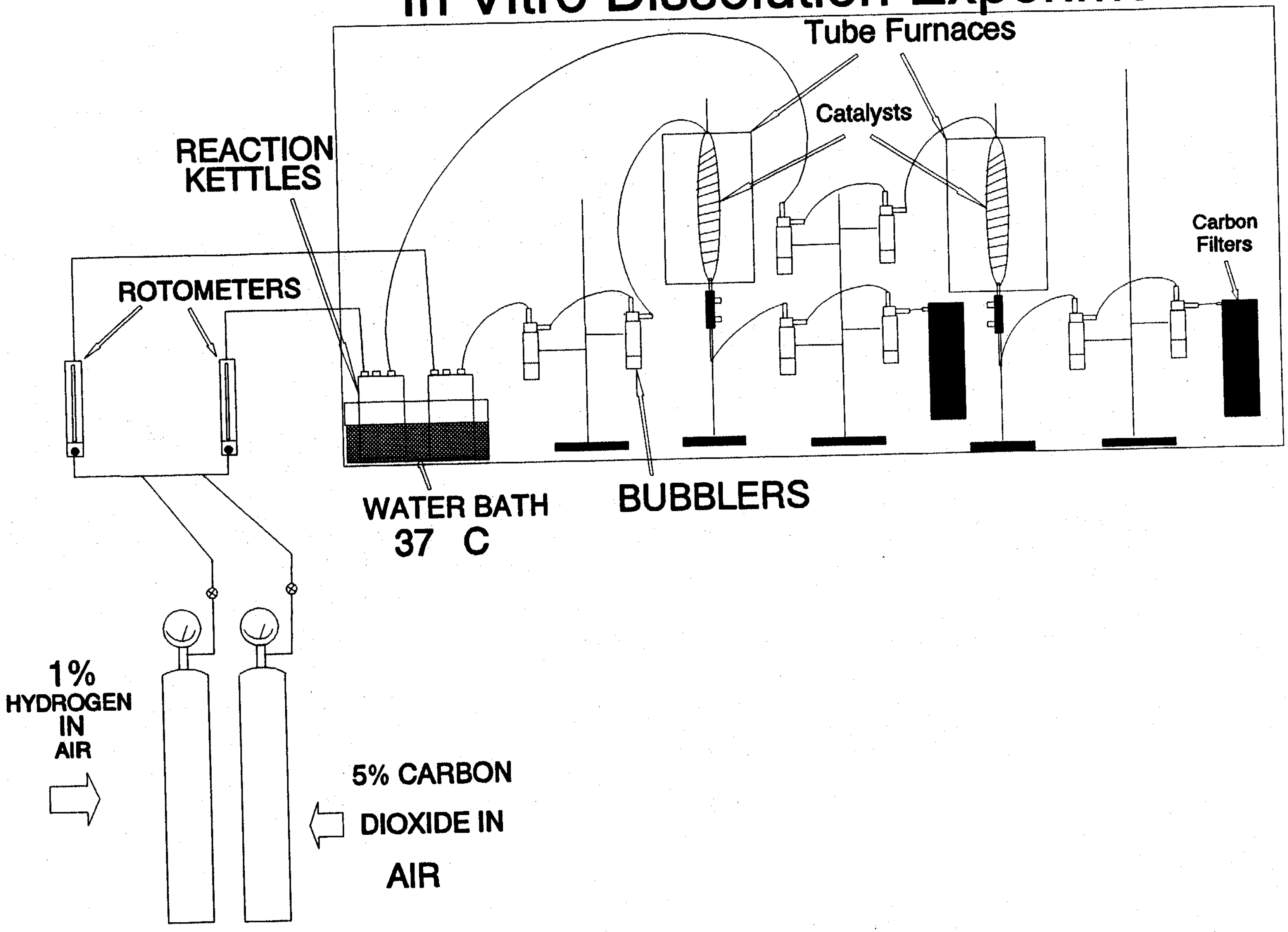
IMAGE ANALYSIS OF TITANIUM TRITIDE PARTICLES
Number of Particles in Sample: 125



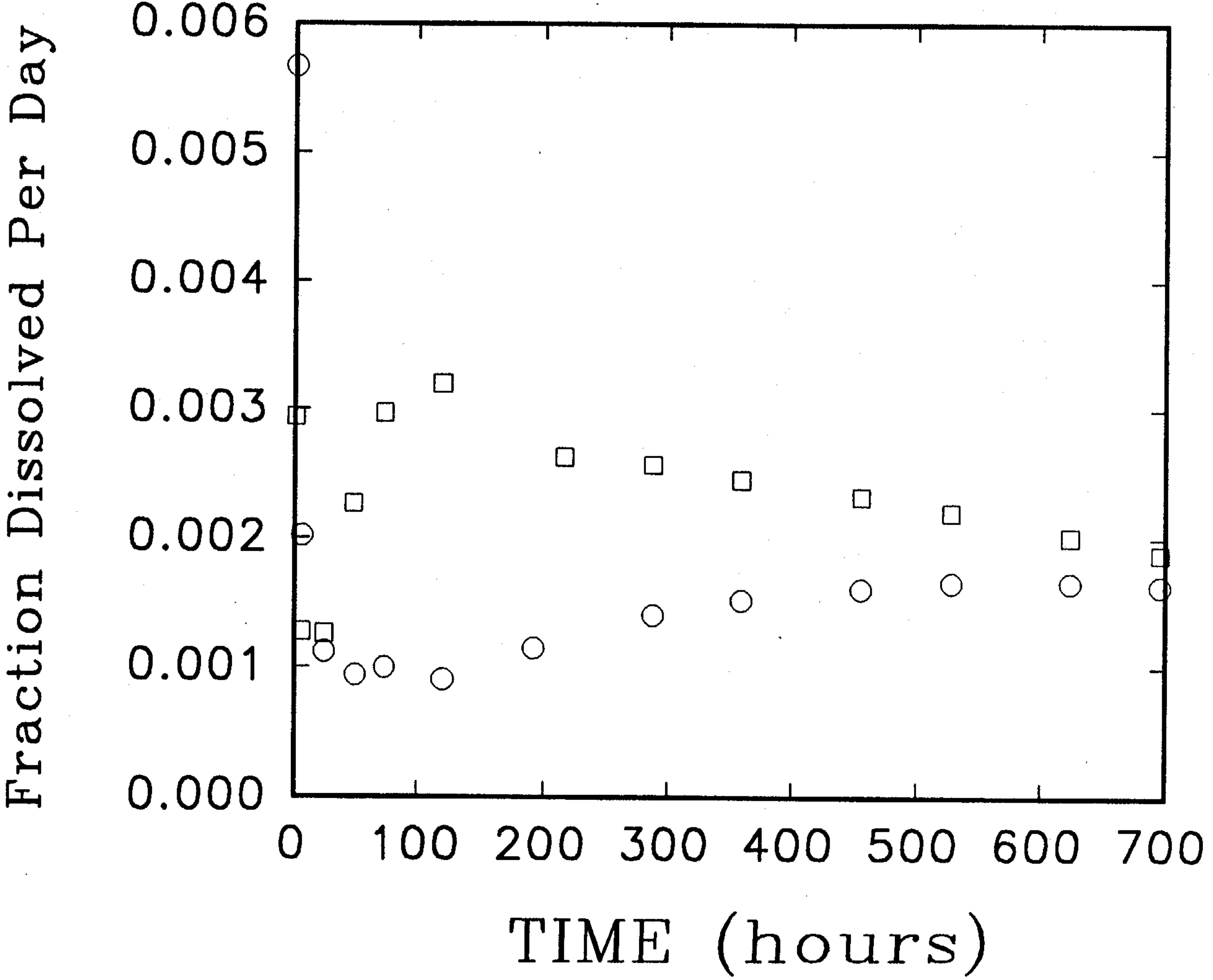
Median Diameter: 103 μm

Standard Deviation: 1.58

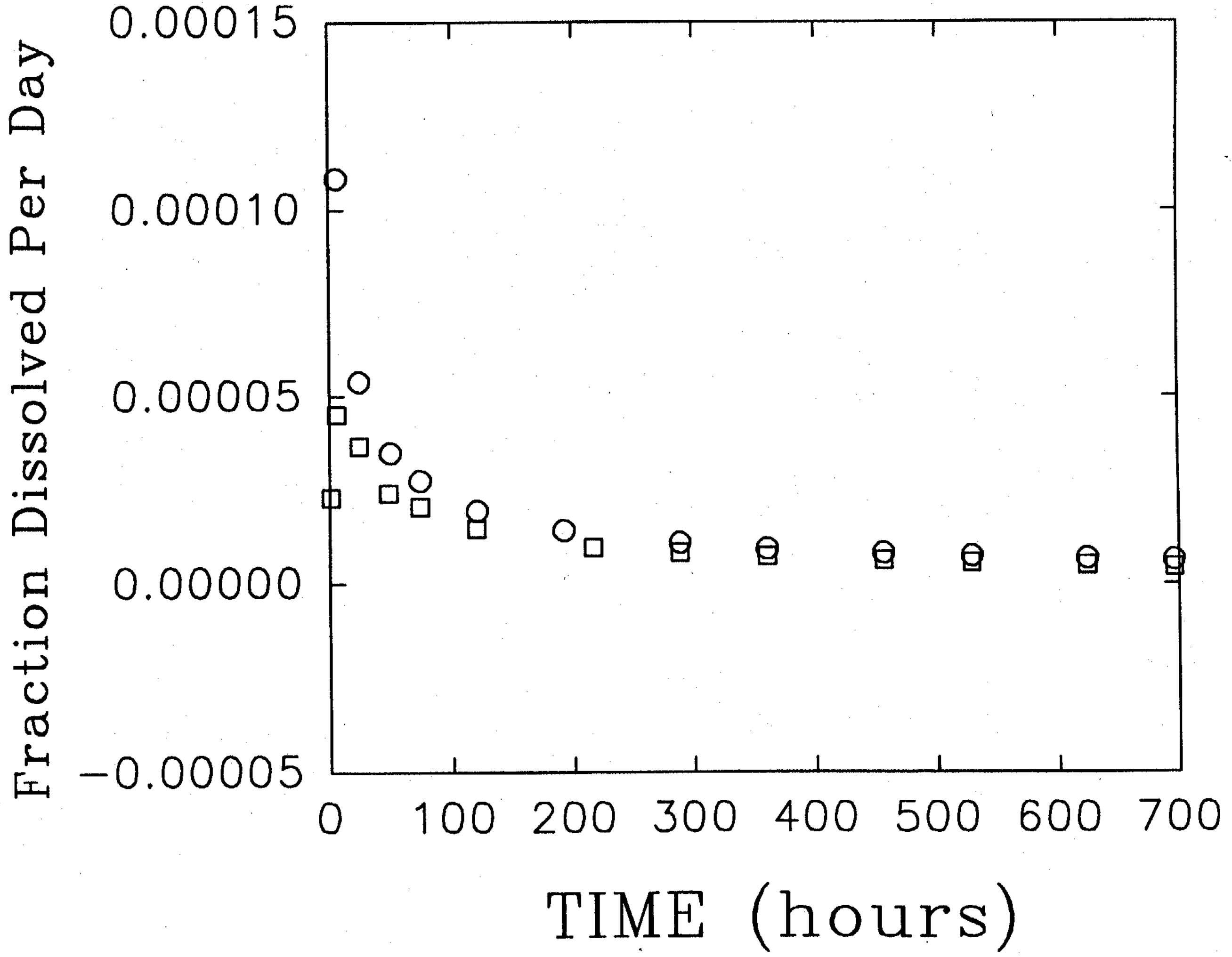
In Vitro Dissolution Experiment



Fraction of Tritium Dissolved Per Day in Solution



Fraction Dissolved Per Day
as Tritium Gas



Titanium Tritide Retention