

1 of 1

**ASSESSMENT OF ACCIDENTAL INTAKES OF URANYL
ACETYLACETONATE (UAA)**

Darrell R. Fisher and James K. Briant
Pacific Northwest Laboratory
Health Physics Department
P.O. Box 999; K3-53
Richland, Washington 99352 U.S.A.

Short title: Assessment of Intakes of UAA

Prepared for presentation at the Workshop on Intakes of Radionuclides:
Detection, Assessment and Limitation of Occupational Exposure;
Bath, United Kingdom, September 13-17, 1993

Abstract -- Uranyl acetylacetonate (UAA) is an organic complex of uranium used for military applications as a chemical catalyst in high explosives. It is prepared from depleted uranium metal (in lots of 5 kg to 7 kg) by dissolution in nitric acid, neutralization, and complexation with 2,4-pentanedione; the precipitate is dissolved in benzene and recrystallized, dried, ground, and packaged. About six workers at a small chemical company were exposed over a period of time to UAA powders during routine preparation and packaging of the uranium catalyst. The dissolution characteristics of the inhaled material were unknown and could not be determined from the published scientific literature. A 1.05-g sample of UAA powder was obtained from the responsible

MASTER

regulatory authority for further study to determine its chemical composition, and for dissolution in simulated lung fluid. We found the solubility of UAA to be equivalent to a mixture of 52% ICRP class D and 48% ICRP class W material. The annual limit on intake and the derived air concentration for radiological protection were estimated from this result for airborne exposure to UAA. A recycling biokinetic model was used to estimate both material-specific variations in urinary excretion rates and lung retention with time after accidental intakes. This study provides new information for evaluating future exposures to UAA.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

INTRODUCTION

Three small chemical companies, under common ownership and operating in the States of Utah and Wyoming (U.S.A.) produced the organic uranium complex uranyl acetylacetonate (UAA) for use as a catalyst in high explosives. Other small chemical companies operating in California and Wisconsin (and perhaps in other locations) have also prepared and shipped UAA crystal to manufacturers of high explosives.

The general radioactive materials license of the Utah company was revoked by the U.S. Nuclear Regulatory Commission in 1988⁽¹⁾ after the owner was cited for withholding the results of elevated levels of uranium in urine of six or more workers involved in routine processing of depleted uranium to produce UAA. The urinalysis results may have indicated that workers received intakes of ^{238}U during grinding, roll-mixing, and packaging of dried UAA crystals and powders.

More than 50% of the urine samples obtained from workers for analysis of uranium were significantly elevated ($>30 \mu\text{g U/L}$) above normal background levels for non-exposed workers (1 to 5 $\mu\text{g U/L}$ by conventional uranium fluorometry). However, not enough samples were obtained from each worker over appropriate time periods for a complete assessment of the amounts of intakes, the retention times, renal tissue exposures to elemental uranium, and radiation doses. It also could not be determined whether the high levels of uranium in the workers' urine resulted from metabolized,

excreted uranium, or from external contamination of the urine specimens. The solubility characteristics of the inhaled material were unknown and could not be determined from the published scientific literature.

The purpose of this study was to analyze UAA for its dissolution rate in simulated lung fluid to determine the retention class of the material that could have been inhaled as an aerosol by the process workers. This information is useful for evaluating the biological retention of UAA in the lungs, its translocation to blood and other organs, and its expected rate of excretion in urine. This information is useful for interpreting bioassay data and assessing internal radiation dose.

PREPARATION OF UAA

A 1.05 g sample of UAA was obtained from the State of Utah, Department of Health, for dissolution testing. This sample was originally obtained as a sample of the final UAA product from one of the companies described above. This sample of uranyl acetylacetonate was originally prepared from depleted uranium rods as follows:

Depleted uranium metal (^{238}U) in lots of 5 kg to 7 kg was dissolved in boiling, concentrated nitric acid (HNO_3). The solution was neutralized by addition of sodium hydroxide (NaOH), forming a crystalline precipitate. 2,4-Pentanedione (acetylacetone, or $\text{C}_5\text{H}_8\text{O}_2$) was added, forming a solution of U(VI) complex as $\text{UO}_2(\text{C}_5\text{H}_8\text{O}_2)_2$ (Figure 1).

Uranyl acetylacetonate was separated from aqueous solution by solvent-extraction in benzene (C_6H_6) heated to 27°C. Bright orange UAA crystals formed in benzene when the solution was allowed to cool and stand overnight. The solvent with any impurities was decanted, and remaining UAA crystals were dried, crushed to fine crystals, and redried to remove residual moisture. Fine UAA crystals were then pulverized in a rolling mixer and packaged for shipping.

DISSOLUTION ANALYSIS

Portions of the Utah UAA sample were subjected to *in vitro* dissolution analysis in simulated lung fluid to determine the rate at which the uranium dissolved. Two representative aliquots of the Utah UAA sample were analyzed in duplicate. Our objective was to analyze aliquots of powder representing respirable material that could have been inhaled and deposited in the lungs of chemical process workers. We determined the UAA sample dissolution rate and averaged the results for each aliquot. The particle-size distribution was not determined.

Preparation of Simulated Lung Fluid

A sterilized simulant of interstitial lung fluid was used to estimate the rate at which particles would dissolve in human lungs. The simulant formula used at our laboratory was previously described by Moss⁽²⁾ and later modified by Briant⁽³⁾

(Table 1). The ingredients listed in Table 1 were added to filtered, de-ionized water.

Particle Dissolution

A small amount of fine UAA powder was collected on two fluoropore teflon air filters (type FG, 0.2 μm , Millipore Corporation, Bedford, Massachusetts) by vacuum suction through air. Teflon was chosen because it is a chemically inert filter material. Each filter was placed in a new filter holder. The active surface was sealed with a 0.1- μm pore diameter Nuclepore® filter (Nuclepore Corporation, Pleasanton, California). The filter holder with sandwiched filter served as the dissolution cell to which 3 mL of simulated lung fluid (described below) was added. Each cell was sealed and placed in a constant-temperature shaker at 37°C (to simulate physiological conditions), as previously described by Briant and James⁽⁴⁾. The teflon filter has a high bubble-point pressure, meaning that a greater pressure than that available would be required for liquid to pass through the filter. Thus, the high bubble-point pressure holds the UAA and the dissolution solution on one side of the filter. The pH of the simulant was maintained between 7.2 and 7.6 by bubbling carbon dioxide (CO_2) through the solution before sealing the dissolution cell.

Fractions of the lung fluid simulant were collected at 1, 2, and 4 hr and at 1, 2, 4, 7, 14, 28, and 56 d after start of the dissolution study. These time points were chosen to provide a geometric progression of sampling times. The lung fluid simulant was

withdrawn from the cell and replaced with fresh simulant at the time each fraction was collected. After withdrawal of the simulant on day 56, the filters were removed from the holder and placed in 8N nitric acid (HNO_3) to dissolve any uranium remaining on the filter.

Uranium Analysis of Dissolution Fractions

The uranium content of each dissolution fraction was measured by laser kinetic phosphorescence analysis (Model KPA-11, Chemchek Instruments, Inc., Richland, Washington). The KPA analyzer was calibrated with a standard uranium solution traceable to the National Institute of Standards and Technology (Gaithersburg, Maryland). The smallest amount of uranium measured in any dissolution fraction (about 10 μg) was several orders of magnitude above the instrument detection limit for uranium (about 0.01 $\mu\text{g/L}$).

RESULTS

Both the short-term and long-term clearance of material in the lungs are influenced by particle dissolution rates. Measuring the dissolution rates allows the material to be classified as retention class D (days), W (weeks), or Y (years) according to the lung model presented in ICRP Publication 30⁽⁵⁾. Inhaled radioactive materials often

consist of mixtures of chemical compounds having differing individual solubilities, and the solubility of a sample, therefore, may be expressed as a combination of classes D, W, and Y retention class.

The amounts (ng/mL) of uranium dissolved from each of two filters were determined for different collection times, and the fractions of the total dissolved per unit time (days) were determined (Table 2). These results were averaged and plotted (Figure 2) to determine lung retention class.

Interpretation of Dissolution Measurements

Data presented in Table 2 were averaged at each time point. Two distinct phases of early dissolution were observed. These early dissolution components were fitted to a two-component exponential function by minimizing the residuals between the fitted curves and the observed data. The remaining material was assumed to dissolve at a single exponential rate, which was the third component of dissolution, and which was determined by the average of the fractions per day of dissolved uranium measured at days 14-56. The dissolution rate constant was calculated by comparison with the amount of uranium left undissolved in the sample. From this we obtained a three-component exponential function of the form:

$$f_{(t)} = 7.841 e^{(-31.09t)} + 0.3448 e^{(-1.293t)} + 0.01394 e^{(-0.02674t)}$$

where $f_{(t)}$ is the rate of dissolution into the lung fluid simulant (fraction per day) and t is time in days. Applying this dissolution rate information to the likely retention of inhaled UAA in the lungs in terms of class D, W, and Y indicated that about 25% of the material could clear the lungs into the circulatory system with a half-time of about 30 minutes, that about 27% could clear with a half-time of about 13 hours, and that the remaining 48% could clear with a half-time of about 26 days. Thus, the UAA was assigned 52% to retention class D and 48% to retention class W.

DISCUSSION

The inhalation of airborne UAA powder may result in lung deposition of depleted uranium (^{238}U). Lung clearance is determined by both particle dissolution and biomechanical clearance (i.e., transport by phagocytic cells and mucociliary action). It appears likely that the UAA material solubility predominates and that a large fraction (approximately 50%) of the uranyl ions (UO_2^{++}) disassociate rapidly in extracellular fluids. The moderately soluble fraction (the remainder) may dissolve from the lungs over a longer time period. Uranyl ions are absorbed into the blood, filtered out by the kidneys, and excreted in urine. Uranium in blood as UO_2^{++} may also be taken up in small amounts by the skeleton, kidneys, and other tissues.

Urinary Excretion Rates

The UAA sample analyzed in this study was found to be best represented as a mixture of class D (52%) and class W (48%) depleted uranium in terms of lung retention. Worker exposure to UAA may be assessed by urinalysis shortly after an intake is suspected. The expected urinary excretion of ^{238}U after a single, acute intake of UAA with this solubility is shown in Figure 3 for the first 50 days after intake. The curve in Figure 3 was obtained using the internal dosimetry computer program CINDY (Version 1.3, available from Canberra Nuclear, Meriden, Connecticut), in which the uranium was assumed to recycle from soft-tissue, bone, kidney, and red blood cell compartments back into the circulatory system according to the Fisher-modified Lipsztein-Wrenn biokinetic model for uranium⁽⁶⁾. This model uses the ICRP Publication 30 respiratory tract model⁽⁵⁾, except that a clearance half-time of 0.03 d (45 min) for the class D pulmonary lung compartment is assumed instead of 0.5 d (12 h).

Lung Retention

The expected lung retention of UAA (52% class D, 48% class W) is shown in Figure 4. The model assumed an activity median aerodynamic diameter (AMAD) of $1.0\ \mu\text{m}$ and that 33% of the acute intake is deposited in the lungs at time of intake.

Annual Limit on Intake (ALI) and Derived Air Concentration (DAC)

The annual limit on intake in ICRP Publication 61⁽⁷⁾ for class D ^{238}U ($f_1 = 0.05$) using ICRP Publication 60 weighting factors⁽⁸⁾ is 9×10^4 Bq, and for class W ^{238}U is 1×10^4 Bq. The annual limit on intake for a UAA mixture composed of 52% class D and 48% class W mixture of UAA would, therefore, be 5×10^4 Bq.

The derived air concentration is $\text{ALI}/2.4 \times 10^3$ (Bq m^{-3}). Therefore, the derived air concentration for a UAA mixture of 52% class D and 48% class W is $5 \times 10^4 \text{ Bq}/2.4 \times 10^3 \text{ m}^3 = 21 \text{ Bq/m}^3$.

Limits for Chemical Protection

The American Conference of Governmental Industrial Hygienists (ACGIH) established a "threshold limit value" (TLV) of 0.2 mg U/m^3 (3 Bq/m^3) for both soluble and insoluble uranium compounds⁽⁹⁾. The U.S. Occupational Safety and Health Administration (OSHA) established a "time-weighted average" (TWA) exposure limit of 0.05 mg U/m^3 (0.7 Bq) for soluble uranium⁽¹⁰⁾. These limits for chemical protection of the kidneys are more restrictive than the ICRP limits for radiological protection.

SUMMARY AND CONCLUSIONS

Uranyl acetylacetonate is a soluble complex of depleted uranium having a bright orange color and industrial application as a chemical catalyst in high explosives. Analysis showed that dissolution of UAA powder in simulated lung fluid followed a three-component exponential function having two rapidly dissolving components and one moderately dissolving component. From this study, the retention characteristic assigned to this material is 52% class D and 48% class W.

Workers involved in production of UAA may be exposed to airborne UAA powders; process workers, therefore, should be protected from potential uranium intakes and monitored by regular urinalysis. The excretion rate curve shown in Figure 3 may be used to estimate a single acute intake from urinalysis results. Workers should also be protected from inhalation of benzene fumes.

The annual limit on intake using ICRP Publication 60 weighting factors is 5×10^4 Bq, and the derived air concentration is 21 Bq/m^3 . The ACGIH threshold limit value of 3 Bq/m^3 and the OSHA time-weighted average exposure limit of 0.7 Bq/m^3 are applicable to depleted uranium as UAA and are more restrictive than the ICRP limits.

ACKNOWLEDGEMENTS

This work was performed for the U.S. Department of Energy and the U.S. Nuclear Regulatory Commission under Contract No. DE-AC06-76RLO 1830. Pacific Northwest Laboratory is operated by Battelle Memorial Institute for the U.S. Department of Energy.

REFERENCES

1. *Federal Register* 53:32125, August 23 (1988); NRC Docket No. 9999004.
2. Moss, O. R. *Simulants of Lung Interstitial Fluid*. *Health Phys.* 36:447-448 (1979).
3. Briant, J. K. Unpublished internal memorandum, Pacific Northwest Laboratory, 11 January (1993). (Note: The concentrations of magnesium chloride and calcium chloride were reduced by 50% from the previously reported values to maintain the solution for long periods of time without crystalline precipitation.)
4. James, J. K. and James, A. C. *Dissolution and Particle Size Characterization of Radioactive Contaminants in Hanford Facilities: Criteria for Methods of Measurement*. PNL-7438 (Pacific Northwest Laboratory, Richland, Washington) (1990).

5. International Commission on Radiological Protection. *Limits for Intakes of Radionuclides by Workers*. ICRP Publication 30 (Oxford: Pergamon Press)(1979).
6. Fisher, D. R., Kathren, R. L., Swint, M. J. *Modified Biokinetic Model for Uranium from Analysis of Acute Exposure to UF₆* Health Phys. 60:335-342 (1991).
7. International Commission on Radiological Protection. *Annual Limits on Intake of Radionuclides by Workers Based on the 1990 Recommendations*. ICRP Publication 61 (Oxford: Pergamon Press)(1991).
8. International Commission on Radiological Protection. *1990 Recommendations of the International Commission on Radiological Protection*. ICRP Publication 60 (Oxford: Pergamon Press)(1991).
9. American Conference of Governmental Industrial Hygienists (ACGIH). *1992-1993 Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices*. (Cincinnati: ACGIH) (1992).
10. *Occupational Safety and Health Standards*. Title 29, Part 1910, *Code of Federal Regulations*, revised July 1, 1992. (Washington, DC: U.S. Government Printing Office) (1992).

Table 1. Simulated Lung Fluid Ingredients

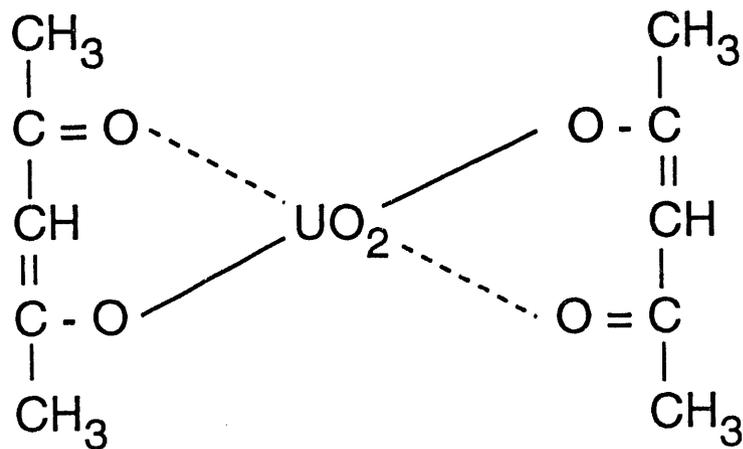
Description		Concentration (g/L water)
Magnesium chloride	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	0.101
Sodium chloride	NaCl	6.019
Potassium chloride	KCl	0.298
Sodium phosphate	$\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$	0.268
Sodium sulfate	Na_2SO_4	0.071
Calcium chloride	$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	0.184
Sodium acetate	$\text{NaH}_3\text{C}_2\text{O}_2 \cdot 3\text{H}_2\text{O}$	0.952
Sodium bicarbonate	NaHCO_3	2.604
Sodium citrate	$\text{Na}_3\text{H}_5\text{C}_6\text{O}_7 \cdot 2\text{H}_2\text{O}$	0.097

**Table 2. Dissolution Rates Measured for Uranium
in Lung Fluid Simulant**

Time Interval	Uranium Dissolved (per day)	
	Filter 1	Filter 2
0-1 hr	4.23	5.05
1-2 hr	0.768	1.61
2-4 hr	0.264	0.595
4-24 hr	0.0977	0.215
1-2 d	0.0255	0.0619
2-4 d	0.0156	0.0262
4-7 d	0.0120	0.0113
7-14 d	0.0170	0.00853
14-28 d	0.0231	0.0119
28-56 d	0.00316	0.00207

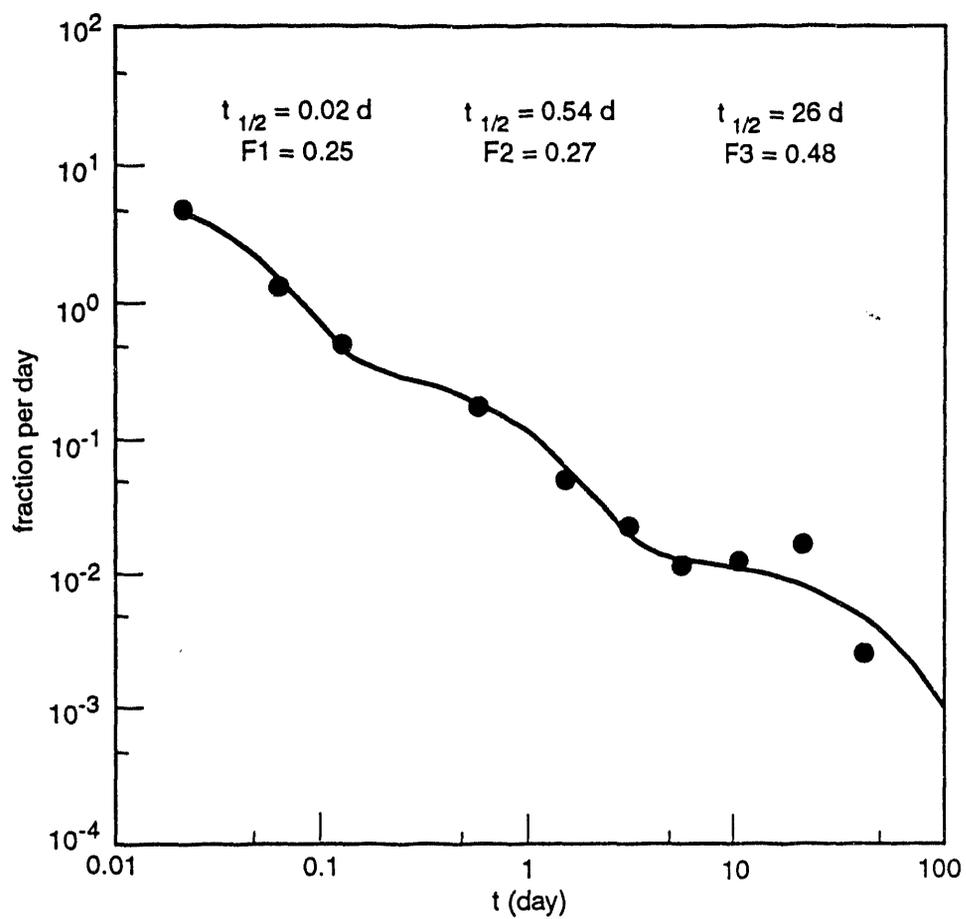
LIST OF FIGURES AND FIGURE CAPTIONS

- Figure 1. Chemical structure of uranyl acetylacetonate (UAA).
- Figure 2. *In vitro* dissolution (fraction per day) of UAA in simulated lung fluid for two samples (averaged).
- Figure 3. Expected urinary excretion rate (fraction per day) of ^{238}U (52% class D, 48% class W) after a single intake.
- Figure 4. Expected lung retention (fraction of single intake) of ^{238}U (52% class D, 48% class W) after a single intake.

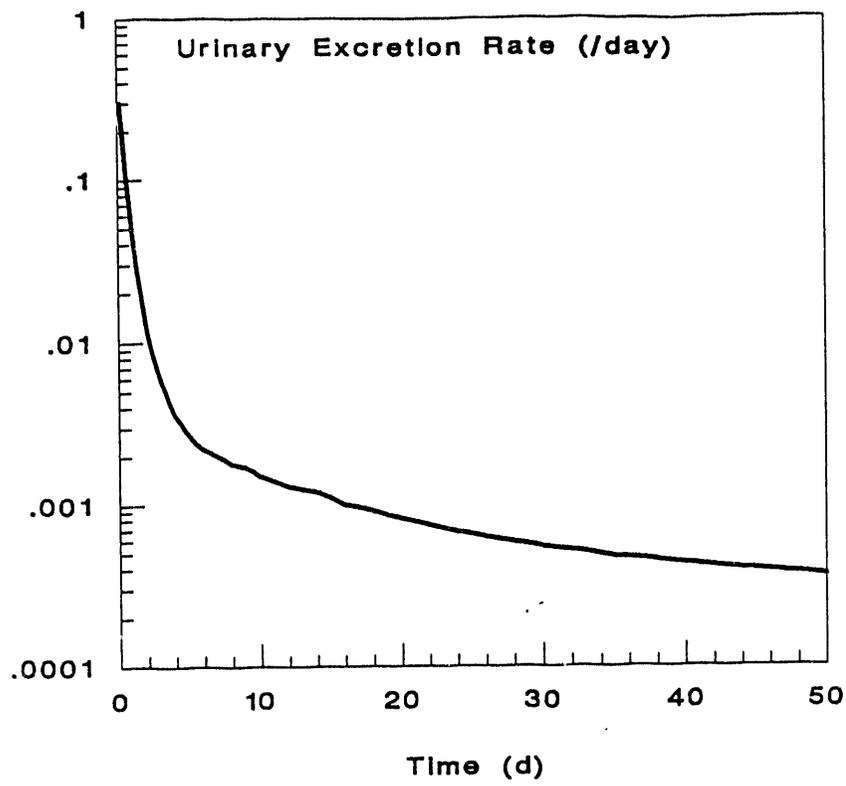


Uranyl Acetylacetonate (UAA)

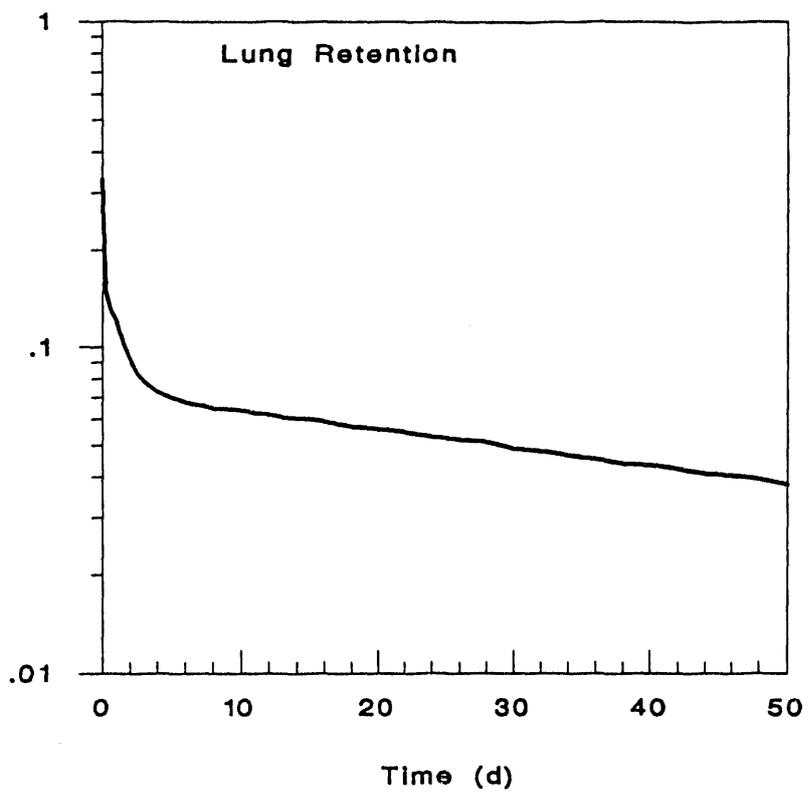
In Vitro Dissolution of UAA in Simulated Lung Fluid



FISHER/BRIANT Figure 2



FISHER/BRIANT Figure 3



FISHER/BRIANT Figure 4

DATE

FILMED

4 / 12 / 94

END

