SAND98-1380C

Self-Irradiation Effects on ^{99}Mo Reagents and Products

S. D. Carson, M. J. McDonald, D. R. Tallant , M. J. Garcia and R.L. Simpson

Sandia National Laboratories*, P.O. Box 5800, Albuquerque, NM 87185

Introduction

In September 1996 the Department of Energy signed a Record of Decision authorizing Sandia National Laboratories in Albuquerque to establish a production capability for ^{99}Mo, the precursor of the medical isotope ^{99m}Tc, and related medical isotopes at its reactor and hot cell facilities. Using the existing facilities, pilot batches of ^{99}Mo that passed industry purity specifications were produced in 1996 and shipped to pharmaceutical houses for evaluation of compatibility with their processes. Once this milestone was achieved, facilities modifications and the Food and Drug Administration validation process for full-scale production were begun. As part of process validation, possible negative effects of the high radiation field produced by ^{99}Mo on both processing reagents and product were considered.

The Problem

Beta irradiation from ^{99}Mo averages 11.2 kGy hr^{-1} (1.12 Mrad hr^{-1}) and can degrade both reagents during isotope separation and the product during shipping. The basic alpha benzoin oxime solution used to precipitate ^{99}Mo as the oxime complex is both air and light-sensitive, and it was felt that reagent behavior in a high radiation field needed to be investigated to ensure that sufficient excess reagent would be used to compensate for any oxime degradation that might occur. In the past, pharmaceutical houses have reported receiving ^{99}Mo product solutions containing a black precipitate that forms during shipment, presumably as a result of self-

* Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

DISCLAIMER

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

irradiation. Addition of sodium hypochlorite to the product solution prior to shipment prevents precipitate formation, indicating the precipitate is a reduced form of ^{99}Mo.

Experimental Procedure

Based on target irradiation time, ^{99}Mo product activity can range from approximately 92 GBq mL^{-1} (2.5 Ci mL^{-1}) to approximately 278 GBq mL^{-1} (7.5 Ci mL^{-1}). The corresponding total dose is 0.17 MGy (17 Mrad) to 1.04 MGy (104 Mrad) for shipping times of 15 to 30 hours. The ^{60}Co source at Sandia's Gamma Irradiation Facility (GIF) produces a field intensity of approximately 12 kGy hr^{-1} (1.2 Mrad hr^{-1}) two inches from the source and was used to determine the effects of irradiation on processing reagents and a simulated product solution of sodium molybdate under a simulated ^{99}Mo radiation environment. Duplicate samples of the acid solution used to dissolve the fission products from the uranium target and the alpha benzoin oxime solution were irradiated for a total of 8 and 4 hours, respectively. These are the maximum times these reagents would be exposed to fission product radiation during ^{99}Mo isolation and purification. Samples of the acid solutions were taken at intervals of 0.5, 1, 4 and 8 hours during irradiation and were titrated with standardized 3N sodium hydroxide to a phenolphthalein endpoint. Oxime degradation was monitored by Fourier transform infrared (FTIR) spectroscopy at 0.5, 1 and 4 hours. FTIR samples were prepared by evaporating aliquots to dryness on barium fluoride plates. Spectra were obtained using a Nicolet Model 800SX spectrometer with a SpectraTech microscope attachment (resolution 8 cm^{-1}.)

Four high density polyethylene (HDPE) product bottles, each containing 80-mL aliquots of a 2% solution of sodium molybdate in 0.2N sodium hydroxide, were also irradiated in the GIF. Bottles were removed after 14.4 hours (sample 1-A, product activity of 92 GBq mL^{-1}, 15 hours shipping time), 28.8 hours (sample 1-B, same activity, 30 hours shipping time), 43.2 hours (sample

1-C, product activity of 278 GBq mL^{-1}, 15 hours shipping time), and 86.4 hours (sample 1-D, same activity, 30 hours shipping time). The molybdate solution was approximately 54 times more concentrated than an average product solution to ensure that, if formed, enough precipitate would be available for isolation and identification. After removal from the GIF, each sample was filtered to remove any precipitate. Duplicate aliquots of the filtered samples were titrated to a phenolphthalein endpoint with standardized 0.2N hydrochloric acid. Unirradiated samples were also titrated prior to irradiation and after standing at room temperature for 86.4 hours. Precipitates were washed to a neutral pH, air dried and analyzed using Raman spectroscopy. Raman spectra were obtained using 514 nm excitation, a triple spectrograph with a charge-coupled-device (CCD) detector and a microscope accessory (~1 μm spatial resolution).

Samples of 2% basic molybdate solution containing sodium hypochlorite were also irradiated and removed at the same time intervals. Since producers of ^{99}Mo normally add 2 mg hypochlorite per 37 GBq (2 mg per Ci) of ^{99}Mo activity, four bottles contained 3.5 mL of 10-13% aqueous sodium hypochlorite (the amount required for 92 GBq mL^{-1}, 80 mL of product) and four contained 10.5 mL (278 GBq mL^{-1}, 80 mL of product).

Results and Discussion

Acid solution

The unirradiated acid solution used to dissolve the fission products contained 3.67 milliequivalents (meq) of acid mL^{-1} of solution, in good agreement with the theoretical value of 3.74 meq mL^{-1} (based on solution composition). No degradation of acid strength was observed after 4 hours of irradiation. After 8 hours, average acid strength was 3.52 meq mL^{-1}, a real decrease of about 4%, but one that is insignificant for processing.

Alpha benzoin oxime

After 0.5 hours of irradiation, the clear, colorless unirradiated oxime solutions had turned pale yellow, but remained clear. After 1 hour, the solutions were a darker yellow and slightly cloudy. After 4 hours, the solutions were yellow ochre and a white precipitate was present. FTIR data for unirradiated alpha benzoin oxime and samples after 0.5, 1 and 4 hours of irradiation are shown in Fig. 1. Due to its inherent instability, the ionization chemistry of alpha benzoin oxime, $C_6H_5CH(OH)C(=NOH)C_6H_5$, would be expected to be quite complex. Initial ionization could reasonably remove a hydrogen from N-OH or homolytically cleave the C=N bond. Either reaction pathway could produce oxidations, cyclizations and/or rearrangements that would ultimately result in a complex product mixture. Since the focus of this investigation was to

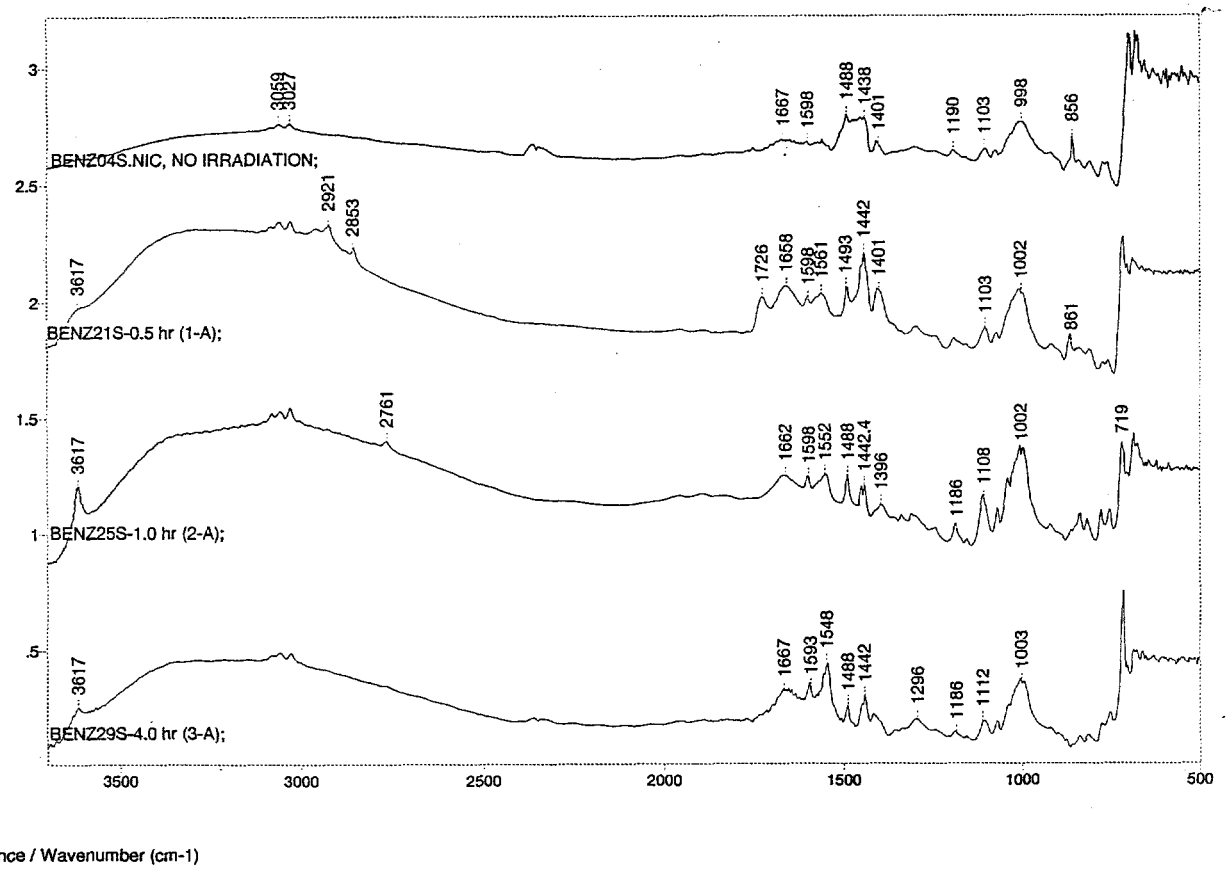

Fig. 1. FTIR data for alpha benzoin oxime after (top to bottom) 0.5, 0, 1 and 4 hours' irradiation.

determine reagent and product stability, no attempt was made to isolate and identify oxime degradation products. However, based on the data in Fig. 1, some generalizations can be made about reactions that may be occurring:

- If a hydrogen atom were abstracted from N-OH, C=N-OH would oxidize to C-NO_2.

Strong evidence for this process is provided by the loss of the 856 cm^{-1} band (N-OH) and the development of an intense band near 1550 cm^{-1}, probably accompanied by a band near 1300 cm^{-1}, and the appearance of a yellow color in irradiated solutions. Organic nitrate compounds are often orange.

- If reaction occurs at the C=N bond, a C=O group would form. The increases in band intensities in the 1550 – 1730 cm^{-1} region may include C=O stretching vibrations from benzoin ($C_6H_5CH(OH)COC_6H_5$, C=O band at 1683 cm^{-1}), benzilic acid, ($(C_6H_5)_2C(OH)CO_2H$, C=O band at 1717 cm^{-1}), and benzil ($C_6H_5COCO\ C_6H_5$, a yellow compound with a C=O band at 1675 cm^{-1}). Further evidence for benzoin is provided by the increase in absorbance in the 3000-3500 cm^{-1} region relative to unirradiated oxime (Fig. 1). Benzoin has a strong, broad OH absorbance that peaks at 3394 cm^{-1}. The 1728 cm-1 peak in the 1-A spectrum in Fig. 1 is a good match in terms of intensity to the 2800-3000 cm-1 C-H bands for the spectrum from an alkane ester.

FTIR analysis of the white precipitate showed it to be alpha benzoin oxime. Since the basic oxime solution is almost saturated at room temperature, it precipitates out of solution as reaction products are formed.

Samples evaporated for FTIR analysis consisted primarily of unreacted oxime with a thin yellow layer of product on top. Based on microscopic examination, it is estimated that less than 10% of the oxime decomposed during 4 hours of irradiation. Since approximately 6.1 times more oxime

is used than is required to complex the maximum amount of ^{99}Mo that could be present , this amount of decomposition is not significant for product isolation.

Molybdate solutions

After 86.4 hours, no precipitate had formed in bottles containing sodium hypochlorite. Black precipitate had formed in all bottles that did not contain sodium hypochlorite after 14.4 hours. The precipitate appeared to initially form on the surface of the HDPE sample bottles and increased steadily with irradiation time. All HDPE bottles turned yellow with time, due to radiation-induced degradation.

Since the precipitate had formed so readily at the high molybdate concentration, three additional sample sets were irradiated:

- Two 80-mL aliquots, each containing 0.145 mmoles of sodium molybdate in 0.2N sodium hydroxide. These samples simulated actual product concentrations.
- Two 25-mL aliquots of the 2% molybdate solution in clear, colorless glass bottles. These were irradiated to determine if HDPE played a role in precipitate formation.
- Two 50-mL aliquots of 0.2N sodium hydroxide in HDPE bottles provided a blank control.

Black precipitate was first noticed in sample set 1 after 28.8 hrs' irradiation. No visible changes were observed in sample sets 2 and 3. After removal from the GIF, 20 mL of each sample containing precipitate was kept at room temperature in the original bottle. Precipitate in these bottles slowly returned to solution. Dissolution times ranged from less than 24 hours for sample 1-A to 4 weeks for sample 1-D. (See Experimental Procedure for sample descriptions.)

Titration data

Titration data were obtained for duplicate 20-mL aliquots of samples 1-A through 1-D and

supplemental sample set 1. Single aliquots were titrated from each bottle in supplemental sample sets 2 and 3. Since no precipitate formed in these bottles, this was equivalent to duplicate samples. Once the precipitate in the 20-mL aliquots that had been set aside had returned to solution, they were also titrated.

The average sodium hydroxide concentration in unirradiated samples was 0.198 meq mL^{-1} and remained constant over the 86.4-hour irradiation period. Samples 1-A, 1-B, supplemental sample sets 1 through 3 and the samples with redissolved precipitate all experienced an average decrease in base strength of 0.013 meq mL^{-1}. Sample 1-C had a decrease of 0.004 meq mL^{-1} and sample 1-D had returned to the initial value of 0.198 meq mL^{-1}.

Raman Data

Raman spectra for the black precipitate from samples 1-C, 1-D and supplemental sample set 1 (samples 1-DIL and 2-DIL) are shown in Fig. 2. The broad bands indicate that the solid is amorphous, most likely composed of a complex mixture of reduced molybdenum oxides, MoO_x, $2<x<3$. All oxides of this type that have been isolated and identified are either brown, black or blue-black (Cotton and Wilkinson 1980) and most are air-sensitive. The two broad regions of Raman bands, 200 – 500 cm^{-1} and 800 – 1000 cm^{-1}, are similar to data obtained by Haro-Poniatowski et al. for amorphous hydrated MoO_3 (Haro-Poniatowski et al. 1998).

What's Happening

The pattern of an initial decrease in pH followed by an apparent increase with increased radiation time and precipitate formation can be explained by considering the primary and secondary reactions that occur in the molybdate product solution due to ionizing radiation. The primary reaction is radiolysis of HDPE, as indicated by the yellowing of the product bottles; the secondary reaction is reduction of the molybdate to the amorphous oxide mixture. The most

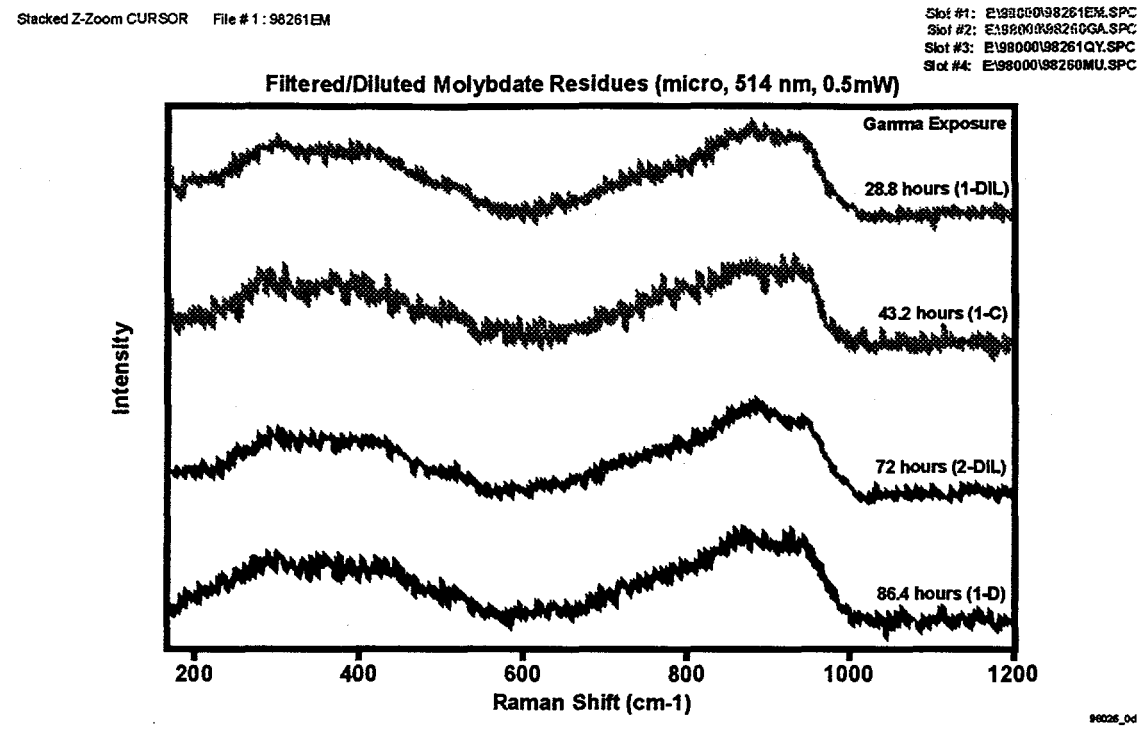

Fig. 2. Raman spectra of the black precipitate formed in ^{99}Mo product solutions after 28.8, 43.2, 72 and 86.4 hours of ^{60}Co irradiation in Sandia's Gamma Irradiation Facility.

common reactions during polymer degradation due to radiolysis are crosslinking and increases in chain unsaturation (Faucette et al. 1993). In HDPE, these processes produce hydrogen gas. Hydrogen that diffuses to the bottle surface will oxidize in the basic product solution, providing electrons that can reduce the molybdate. The oxidation of hydrogen accounts for the decrease in base concentration that occurs in the blank sodium hydroxide solution as well as initially in the molybdate solutions. The subsequent molybdate reduction will cause the base concentration to increase with time, as seen in the titration of 1-C and 1-D samples. The precipitate does not form in solutions containing sodium hypochlorite because the latter is a strong oxidizing agent that reacts to keep the molybdenum in its highest oxidation state. Because the molybdenum oxides that form are unstable in air, they slowly oxidize to stable molybdenum trioxide, which

dissolves in base to produce the molybdate anion. The observed disappearance of the black precipitate over time accompanied by a decrease in solution base strength is consistent with this process.

The primary ionizing radiation reaction in aqueous solutions that contain solute at concentrations ≤0.1 M is water radiolysis (Ferradini 1961). The molar concentration of the 2% sodium molybdate solution is approximately 0.08 M; therefore, direct interaction between the radiation and the molybdate is unlikely. While hydrogen production from water radiolysis is approximately ten times less efficient than HDPE radiolysis (Ferradini 1961), one would still expect to see precipitate in the glass bottles. The fact that no precipitate is observed when the molybdate solution is irradiated in a glass bottle can be explained by reaction kinetics. The rate constant for hydrogen production in irradiated water is 1.5×10^8 $M^{-1}sec^{-1}$; for peroxide production it is 2×10^8 $M^{-1}sec^{-1}$ (Ferradini 1961). Approximately equivalent rates of formation and the reaction stoichiometry argue that the steady-state concentrations of hydrogen and peroxide in solution will be roughly equal. While the hydrogen can reduce the molybdate, hydrogen peroxide is an effective oxidizing agent. If the rate of molybdate reduction by hydrogen is approximately equal to the rate of oxide oxidation by peroxide, no precipitate would be observed in the absence of any source of hydrogen other than water radiolysis. The fact that no precipitate is observed in a glass container is an indication that the rates of molybdenum oxidation and reduction are comparable.

Summary

The acid and oxime solutions used to isolate ^{99}Mo are not significantly degraded by fission product radiation. Hydrogen gas produced from radiolysis of the HDPE product bottle is oxidized at the bottle's surface by the hydroxide present in the product solution. This provides a

source of electrons for reduction of molybdenum from the +6 oxidation state of the molybdate anion that is normally present in basic solution. The reduced molybdenum forms a black amorphous precipitate of mixed oxides, MoO_x, $2<x<3$. Since the oxides are unstable in air, they slowly re-oxidize to molybdenum trioxide, which dissolves in the sodium hydroxide to regenerate the molybdate anion. The addition of sodium hypochlorite, a strong oxidizing agent, effectively prevents precipitate formation.

The kinetics and thermodynamics of the basic molybdate solution radiation chemistry are such that precipitate does not form when the solution is in a glass bottle. A hydrogen source other than water, in this case HDPE, is necessary for precipitate formation.

References

Faucette, A. M.; Logsdon, B. W.; Oldham, J. H. A review of the radioactive and thermal stability of low density polyethylene encapsulated nitrate salt waste. In: Proceedings of Waste Management '93, vol 2. Tucson: 1993:1833-1837.

Ferradini, C. Kinetic behavior of the radiolysis products of water. In: Advances in inorganic chemistry and radiochemistry, vol 3. New York: Academic Press; 1961: 171-204.

Haro-Poniatowski, E.; Julien, C.; Pecquenard, B.; Livage, J.; Camacho-Lopez, M. A. Laser-induced structural transformations in MoO_3 investigated by Raman spectroscopy. J. Mater. Res. 13:1033-1037; 1998.

Roberts, J. D.; Caserio, M. C. Basic principles of organic chemistry. Third printing. New York: W. A. Benjamin; 1965: 495.