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Irradiation of HDPE Bottles

Chemical Sciences and Engineering Division

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IRRADIATION OF HDPE BOTTLES

1 INTRODUCTION

The short-term plan of NorthStar Medical Technologies for production of Mo-99 is to use the research reactor at the University of Missouri in Columbia (MURR). The Mo-99 will be produced by the activation reaction Mo-98(n,γ)Mo-99 using enriched Mo-98 targets. There is a concern about the radiation stability of the high-density polyethylene (HDPE) bottles to be used to move the Mo product from the MURR recovery hot cell to the dispensing cell. Therefore, Argonne performed an experimental study to measure the radiation stability of the HDPE bottles, which can be used to transfer ~450 Ci of Mo-99. The first part of the study was to calculate that the dose the bottle will receive over two weeks with starting activity of 450 Ci of Mo-99. Then, irradiation experiments were performed with a Van de Graaff electron generator.

2 ESTIMATION OF DOSE FOR HDPE BOTTLE

The general purpose Monte Carlo particle transport code (MCNPX) was used to model the dose absorbed in a HDPE container from 450 Ci (1500 mL with 300 mCi/mL) of the Mo-99 source (in equilibrium with Tc-99m) in a 5 M KOH solution. Power (and dose) deposition was treated in separate simulations for beta and gamma radiation sources. Source particles were sampled uniformly inside the solution volume with appropriate energy distributions (continuous for beta and discrete energy lines for gamma radiation). The weights for the source particles were set such that they matched the strength (particles/sec) of a 450 Ci Mo-99 source. Total heating (tally type 6 [MeV/g] per source particle) was converted to absorbed dose rate (rad/hr) and absorbed power (W), and the dose rates were tallied for the solution, container body, and container cap. The results for the initial source activity (450 Ci) are summarized in Table 1 and plotted in Figure 1.

Decay-corrected integrated absorbed dose in the HDPE bottle in two weeks of exposure time was also calculated for each source of radiation. This was done by multiplying Table 1 values by $(1 - \exp(-\lambda t))/\lambda$, where λ is the decay constant of Mo-99, and t is the decay period of two weeks. These results are presented in Table 2. Based on the dose rate results, the total dose to the bottle (from all sources) amounts to 3.17 Mrad.

TABLE 1 Dose Rate Results Calculated from MCNPX Code

	Bottle	Cap	Solution
	Dose Rate [krad/hr]		
Mo-99 beta	21.0	3.9	164.5
Mo-99 gamma	9.9	2.4	37.5
Tc-99m gamma	3.5	0.8	24.5
Total	34.4	7.0	226.6

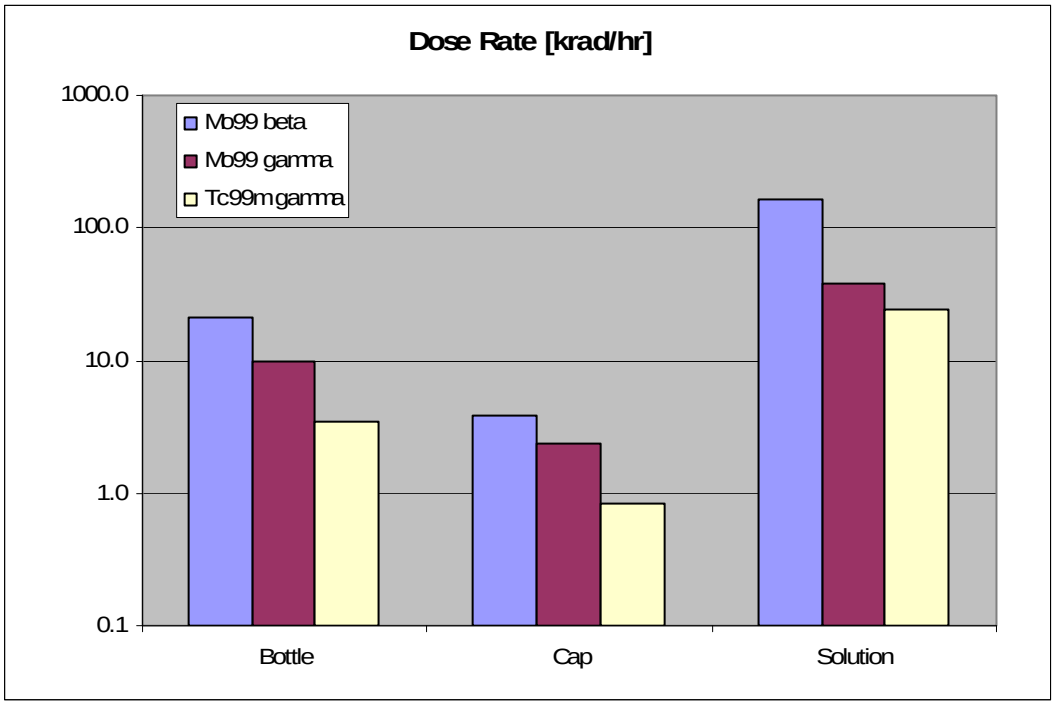

FIGURE 1 Dose Rates Calculated from MCNPX code

TABLE 2 Total Absorbed Dose in the Bottle

	Total Dose in Two Weeks
	[Mrad]
Mo99 beta	1.94
Mo99 gamma	0.91
Tc99m gamma	0.32
Total	3.17

3 DETERMINATION OF THE BEAM PARAMETERS AND DOSE RATE

An electron-beam profile of Van de Graaff (VDG) generator at a 10 μA beam and 25 in. from the beam window was determined using a Faraday cup. The difference in current on the bottle at different heights is shown in Figure 2. The beam profile is not dependent on the beam current. The setup for irradiation of HDPE bottles is shown in Figure 3.

The dose rate delivered by a 20 μA beam at 25 in. from the beam window was determined with an oxalic acid dosimeter [1]. In a series of experiments, an HDPE bottle was filled with 90-100 mL of 0.6 M oxalic acid and irradiated for different times while being rotated. The concentration of oxalic acid remaining after irradiation of the solution was determined by potentiometric titration with a standardized 0.2 M NaOH. The dose was calculated for a decomposition of less than 30% of the initial concentration of oxalic acid by a standard procedure with a radiochemical yield of G = 4.9 [1]. The dose can be calculated irrespective of the change in oxalic acid concentration with the equation:

$$\log D = a \log C + b \qquad \text{eq. 1}$$

where D is the absorbed dose in eV/mL; C is the number of oxalic acid molecules decomposed in l ml; and a=0.999 and b=1.344 are constants that depend on the initial concentration of oxalic

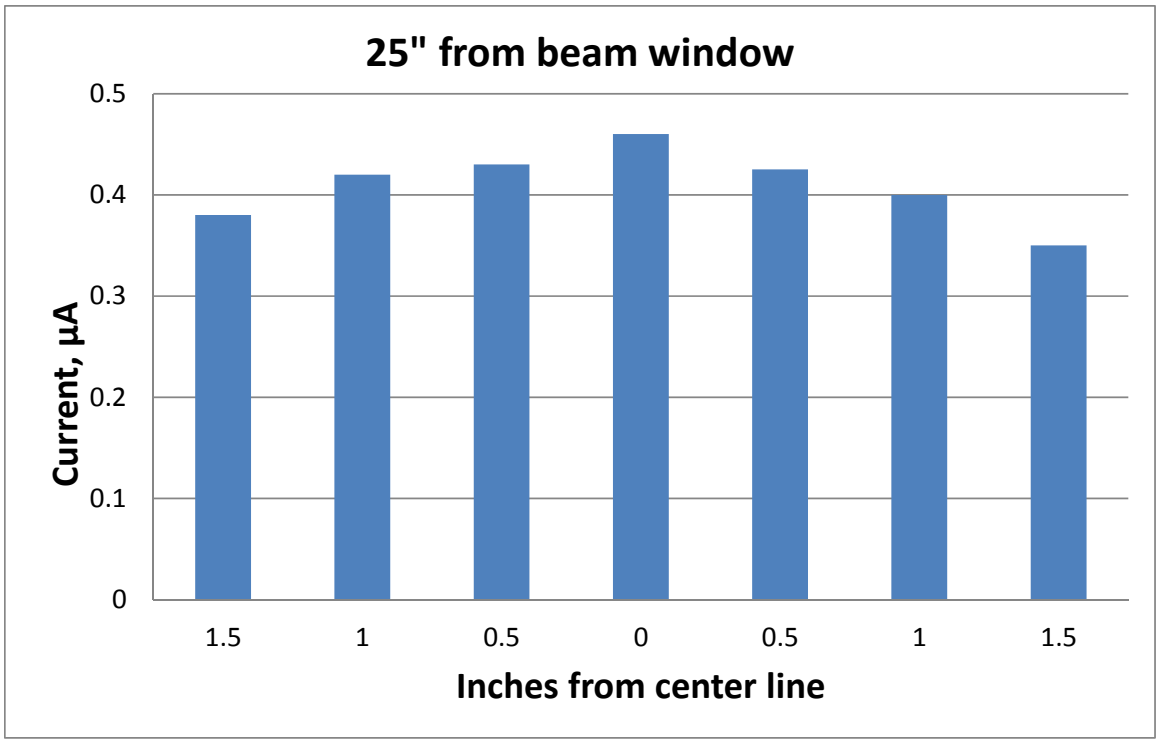

FIGURE 2 Profile of 10 μA Shutter Current Beam at 25 in. from Window and Various Distances from Center Line

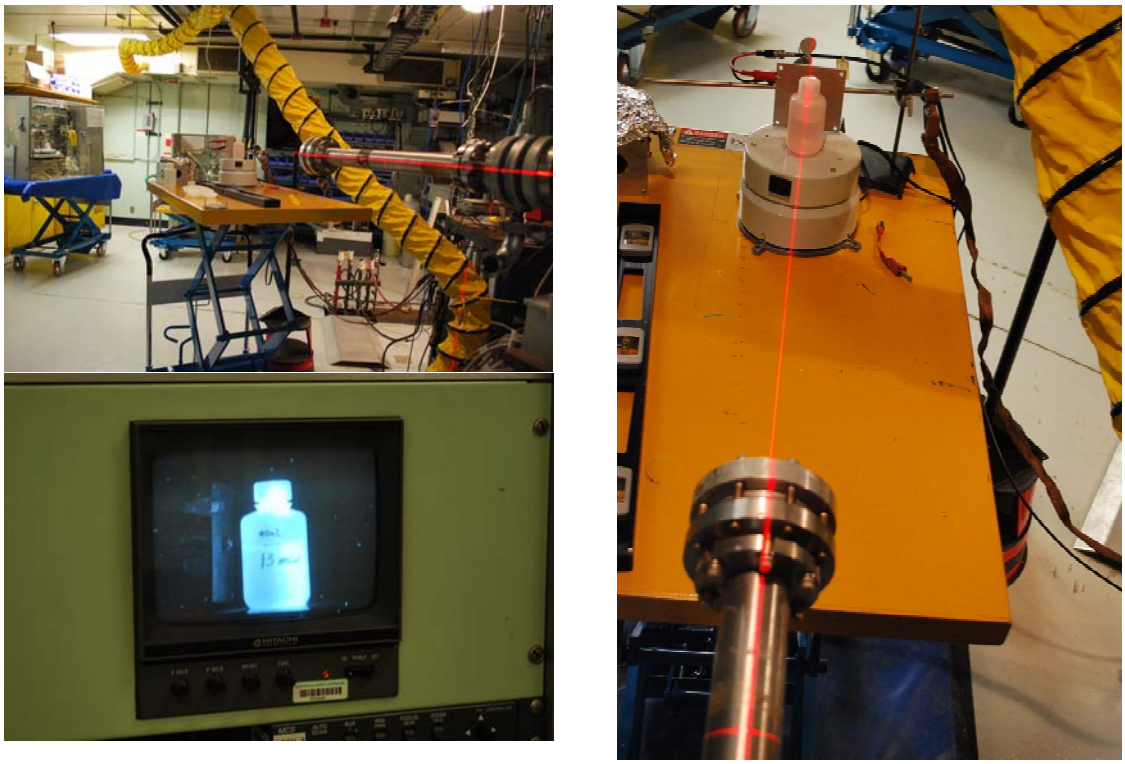

FIGURE 3 Setup for the Irradiation of HDPE Bottles. During the irradiation, bottles were filled with K_2MoO_4 in 5 M KOH (0.2 g-Mo/mL) and were rotated to achieve an even dose rate throughout.

acid (0.6 M) and the number of oxalic acid molecules decomposed. A plot of dose versus time (both current and time were monitored) up to 30 min yielded a linear relationship, as shown in Figure 4. Based on the data from Figure 4, the dose rate for the irradiation of the HDPE bottles with 20 μA shutter electron beam at 25 in. from the window is 0.247 Mrad/min.

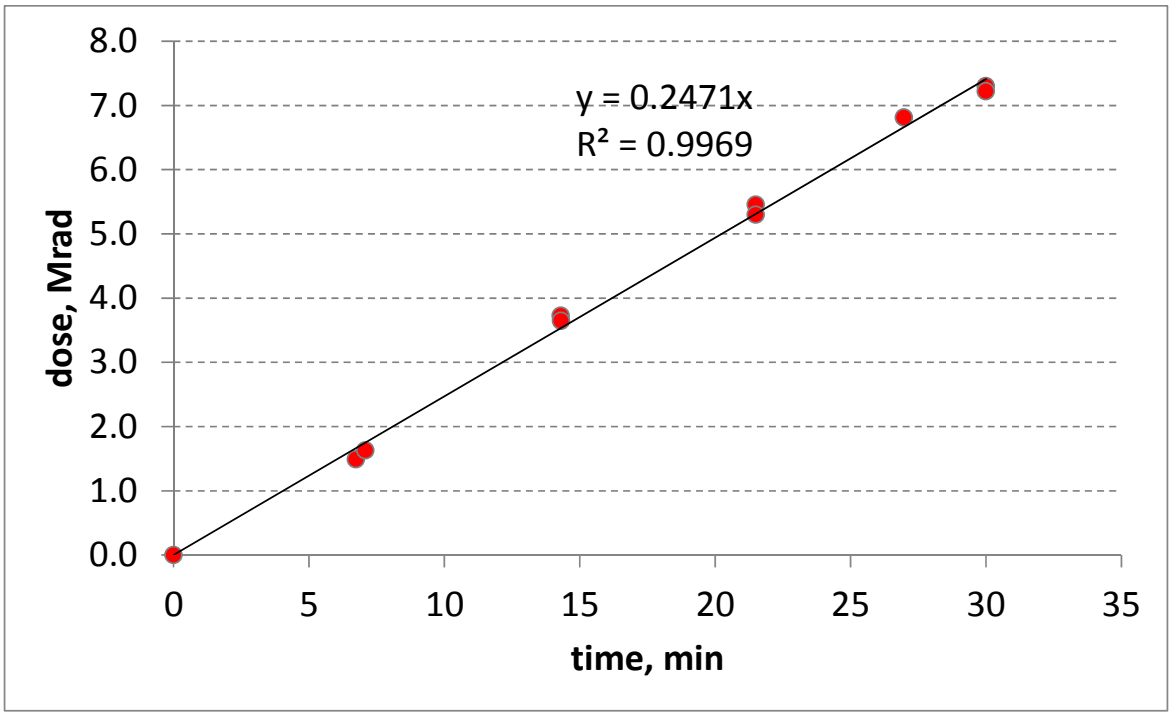

FIGURE 4 Linear Relationship between the Time and Dose Determined from the Irradiation of 90-100 mL of 0.6 M Oxalic Acid with 20 µA Shutter Electron Beam at 25 in. from the Window

4 IRRADIATIONS OF HDPE BOTTLES

Three sets of bottles were irradiated with the VDG, and general information about them is listed in Table 3.

It should be noted that the VWR bottles in Experiment 1 (Table 3) were made of softer HDPE material than the Nalgene bottles. The VWR bottles in Experiment 1 received doses of 0.124, 1.42, 3.31, and 15.35 Mrad and are being analyzed by NorthStar.

The Nalgene bottles in Experiment 2 received doses of 0.74, 1.46, 2.98, and 5.99 Mrad. Figure 5 is a photograph of the irradiated bottles from Experiment 2.

TABLE 3 General Information for HDPE Bottle Irradiation Using the VDG

#	Bottle	Brand (part number)	Mouth	K_2MoO_4 in 5M KOH	KNO_3
1	HDPE + PP cap	VWR (16059-068)	narrow	0.2 g-Mo/mL	-
2	HDPE + PP cap	Nalgene (2002-0004)	narrow	0.2 g-Mo/mL	-
3	HDPE + PP cap	Nalgene (312104-0002)	wide	0.2 g-Mo/mL	0.12M

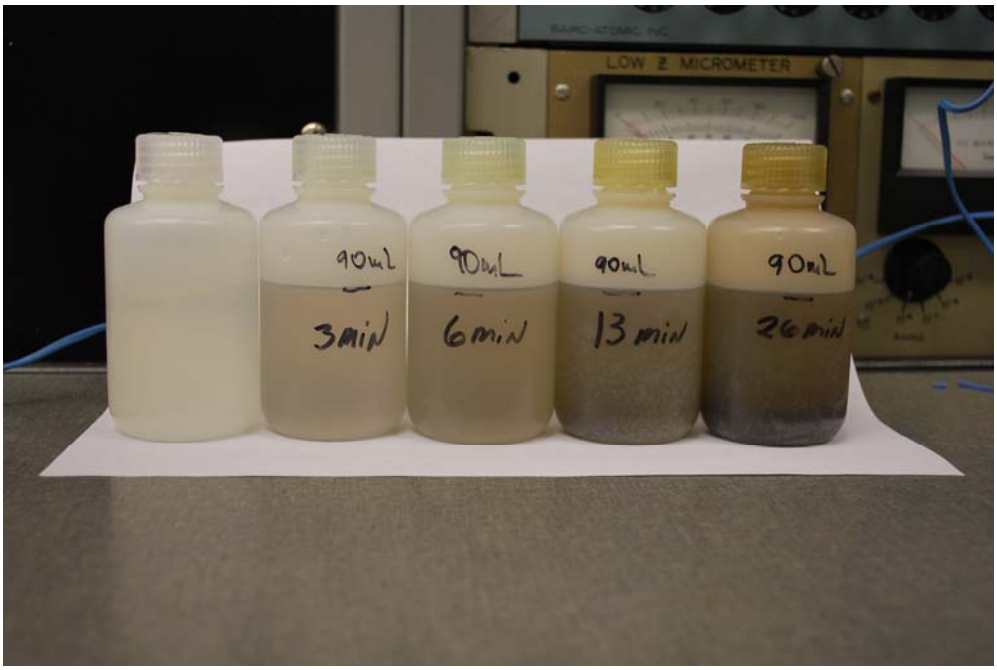

FIGURE 5 Picture of Irradiated HDPE Bottles Containing K_2MoO_4 in 5M KOH (0.2 g-Mo/mL). Bottle on very left is non-irradiated bottle containing K_2MoO_4 in 5M KOH

As the irradiation time increases, the coloration of bottles is obvious and was expected; however, the solution of K_2MoO_4 in 5 M KOH turned brown as well. Over time, a brown precipitate formed. The brown precipitate was filtered through fine filter and extensively washed with deionized water. After washing, the precipitate was re-dissolved using a 1:1 mixture of HCl/HNO_3 (Figure 6), and the sample submitted for inductively coupled plasma mass spectrometry (ICP-MS) analysis. The sample was tested for molybdenum and common impurities that could be present in starting material used to prepare Mo solution. The ICP-MS analysis of the brown precipitate (Table 4) shows that the major component was Mo (86.2%), indicating reduction of Mo(VI) to MoO_2. Other elements identified included Ca (5.9%), Al (4%), Si (1.8%), and Fe (1.1%). It should be noted that the concentration of oxygen cannot be determined by ICP-MS, but it represents 25% of the MoO_2 mass. This would slightly affect the distribution of major elements determined in the brown precipitate.

Visual inspection of irradiated bottles revealed a cracked cap on the bottle irradiated at the highest dose (15.35 Mrad). The solution from damaged bottles was transferred into a new bottle, and the bottle with the cracked cap was sent to NorthStar for examination together with other irradiated bottles containing solution.

FIGURE 6 Photographs of Brown Precipitate Collected on the Fritted Funnel (left) and Solution Formed after Dissolution of Precipitate in 1:1 Mixture of HCl/HNO_3 (right)

TABLE 4 ICP-MS Results for Composition of Brown Precipitate

Element	Relative Composition
Mo	86.2%
Ca	5.9%
Al	4.0%
Si	1.8%
Fe	1.1%
Cu	0.363%
Cr	0.353%
Cd	0.141%
Ti	0.061%
W	0.052%
Mn	0.046%
Sn	0.044%
Sb	0.023%
Nb	0.004%
Rb	0.002%
Te	0.000%

A third set of irradiations (Table 3) was performed with wide-mouth HDPE bottles containing 100 mL of K_2MoO_4 in 5 M KOH with 0.12 M KNO_3. The bottles received doses of 0.12, 0.74, 1.42, 2.2, 3.2, 6.5, and 14.6 Mrad. Figure 7 is a photograph of the irradiated bottles. The irradiated solutions remained colorless, and no precipitate was observed even after prolonged time. Experiments showed that the presence of an oxidizer, such as KNO_3, is necessary to avoid reduction of Mo and formation of precipitate due to radiolysis. All irradiated HDPE bottles containing Mo solution were sent to NorthStar for testing.

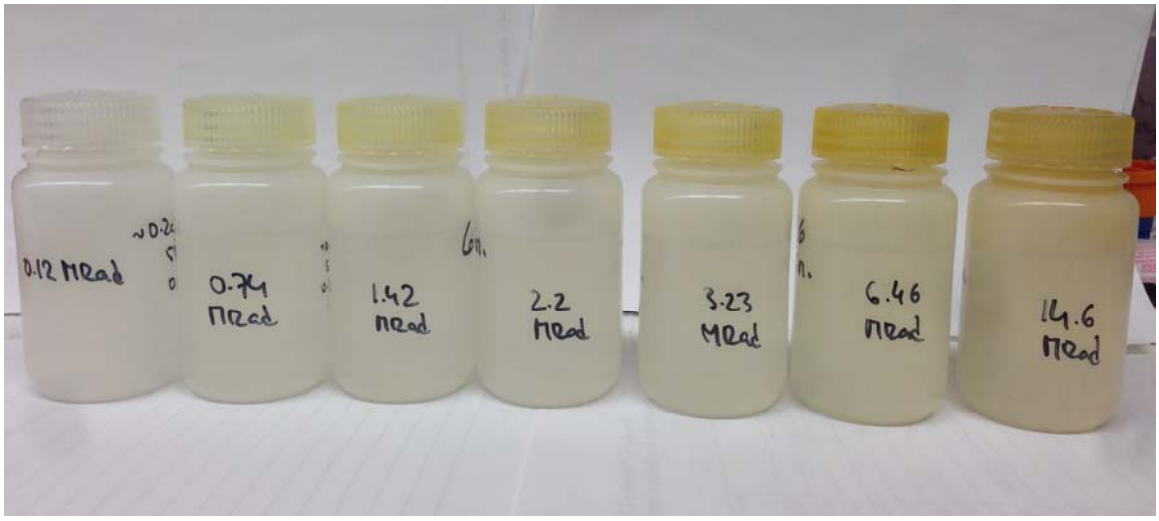

FIGURE 7 Photograph of Irradiated HDPE Bottles Containing K_2MoO_4 in 5 M KOH (0.2 g-Mo/mL) with 0.12 M KNO_3

5 SUMMARY

Monte Carlo calculations were performed using the MCNPX code to estimate doses delivered to HDPE bottles containing 450 Ci of Mo-99 in K_2MoO_4 solution in 5M KOH (0.2 g-Mo/mL). Based on the calculations, the total estimated dose absorbed by the HDPE bottles in two weeks is ~3.17 Mrad. To check the radiolytic stability of the HDPE bottles, irradiation studies were performed using the electron beam of a Van de Graaff generator.

As the delivered dose increased, the bottles turned noticeably brown. Moreover, the solution of K_2MoO_4 in 5 M KOH turned brown as well. Over time, a brown precipitate formed. A sample of this precipitate was analyzed by ICP-MS and showed the major component of the precipitate to be Mo. This product was due to radiolytic reduction of Mo and formation of insoluble MoO_2. Irradiations performed in the presence of 0.12 M KNO_3 prevented the radiolytic reduction of Mo, and no precipitate was observed even after prolonged time. Experiments showed that the presence of an oxidizer, such as KNO_3, is necessary to avoid reduction of Mo and formation of precipitate due to radiolysis. The irradiated bottles were shipped to NorthStar for analysis.

6 REFERENCE

[1] I. Draganic, “Oxalic Acid: The Only Aqueous Dosimeter for In-Pile Use,” *Nucleonics* **21**(2), 1963.

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