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Radiolytic Stability of the ABEC Column

Chemical Science and Engineering Division

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by
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RADIOLYTIC STABILITY OF THE ABEC COLUMN

1 INTRODUCTION

A key reagent of the TechneGen generator (NorthStar) is an ABEC (aqueous biphasic extraction chromatographic) column that consists of polyethylene glycol (PEG) bonded to a polystyrene-divinylbenzene co-polymer bead. The ABEC column is highly selective for the pertechnetate ion under highly alkaline conditions, while molybdenum passes through the column. This study was focused on determining whether radiolysis of an ABEC column used multiple times in a 20-Ci (Mo-99) generator could affect the recovery of technetium due to a radiolytic degradation of PEG. Irradiations were performed using a Van de Graaff generator.

2 ESTIMATION OF DOSE FOR THE ABEC COLUMN USING MCNPX

Monte Carlo calculations have been performed using MCNPX (Monte Carlo N-Particle eXtended) to estimate doses delivered to a 1.6-mL ABEC column during seven loadings (one every day) of a TechneGen generator with 20 Ci (at the first day) of Mo-99 in a 20-mL solution of 5-M KOH (1 Ci of Mo-99/mL). The dead volume of the ABEC column was determined to be around 250 µL (15–16%). Based on the dead volume, 250 mCi (first loading) of Mo-99 was uniformly distributed as a source in the entire column; all 20 Ci of Tc-99m source was placed in the top third of the column. A schematic description of the simulation model is presented in Figure 1.

Beta and gamma dose contributions from the Mo-99 source, along with the gamma dose of the Tc-99m, were calculated and plotted for each loading. The resulting plot is shown in Figure 2. The plot demonstrates that the major component in the total dose is the dose deposited by beta particles emitted from the decay of Mo-99. This beta dose is far more significant than the combined gamma dose from Mo-99 and Tc-99m, because (1) all beta energy is deposited inside the column and (2) only a small fraction of the gamma energy deposited inside the column. The reason the Tc-99m gamma dose is much more significant than the Mo-99 gamma dose is that the full amount of Tc-99m is assumed to be absorbed in the top third of the column, while Mo-99 activity is distributed uniformly in the liquid phase, which occupies 15% of the column volume. Calculations assume that Mo-99 is present in the column for 42 minutes (per loading), whereas the Tc-99m dose lasted for approximately 21 minutes, because it is linearly accumulated on the column over the entire loading and washing process.

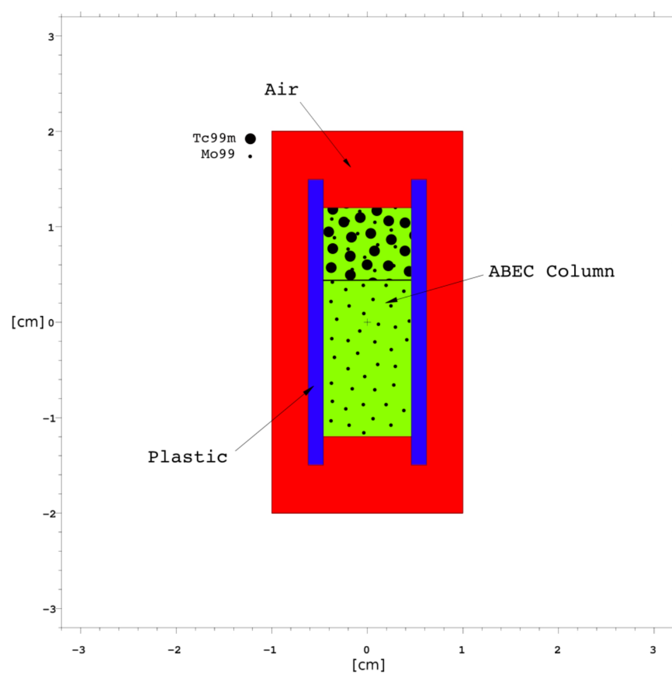

FIGURE 1 A Schematic Illustration of the MCNPX Model Geometry

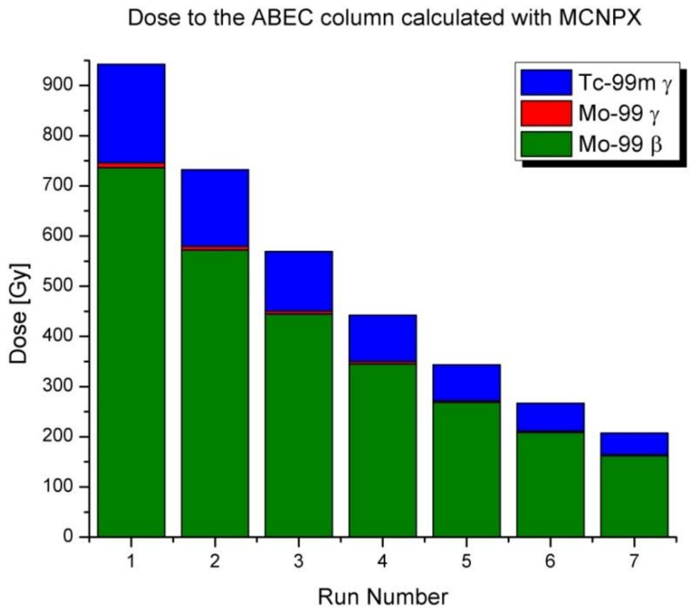

FIGURE 2 Calculated Mo-99 (beta and gamma) and Tc-99m (gamma) Doses as a Function of Loading Run Number (Total integrated doses for the seven loadings have also been calculated; the results are presented as a pie chart in Figure 3. The chart shows 2.737 kGy, 0.036 kGy, and 0.73 kGy, respectively, from Mo-99 beta, Mo-99 gamma, and Tc-99m gamma cumulative doses. This amounts to the total dose of 3.5 kGy.)

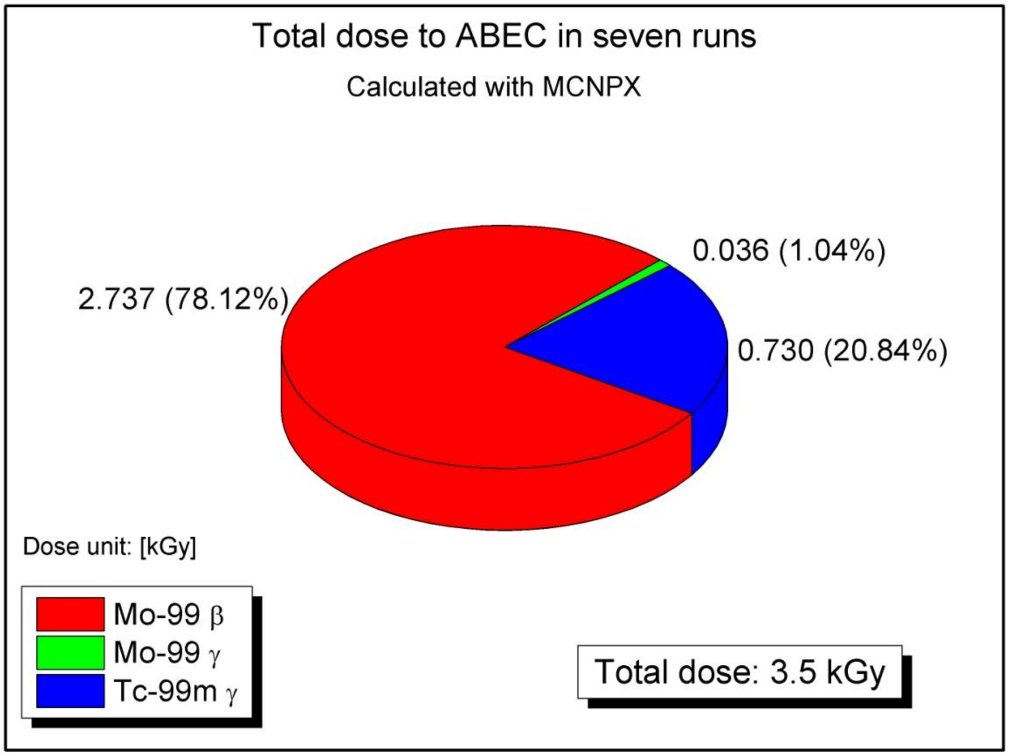

FIGURE 3 Cumulative Doses of Mo-99 (beta and gamma) and Tc-99m (gamma) Deposited as a Result of Seven Consecutive Loadings (one every day) of the ABEC Column

3 DETERMINATION OF THE BEAM PARAMETERS AND DOSE RATE

The electron beam profile of the Van de Graaff generator at the 18-µA beam and at various distances from the window was determined using a Faraday cup. The current on the column was in the range of 0.21–0.34 µA. The results at three different distances are shown in Figure 4. The setup for irradiation of an ABEC column is shown in Figure 5. Prior to the actual irradiation of the ABEC columns, the temperature in the center of the column (filled with polystyrene polymer only) was determined using a thermocouple wire at column distances at 20, 18, and 16 in. from the beam window while pumping a solution of 5-M KOH through it. The temperature was 26.4°C at 20 in., 26.5°C at 18 in., and 30.0°C at 16 in. Based on the beam profile and temperature data, the distance of 20 in. was chosen for the irradiation of the ABEC columns.

At 20 in., the difference in beam current within a half inch of the center of the beam was less than 5%, which provides a homogenous dose profile in the column. The temperature of the column during the irradiation at 20 in. (~26.4°C) was acceptable to NorthStar.

The dose rate delivered by the 18-µA beam at 20 in. from the window was determined using oxalic acid dosimeter (Draganic 1963). A series of experiments were performed, in which an empty column identical in size to the ABEC column was filled with 1.5 mL of 0.6-M oxalic acid and irradiated for different amounts of time while being rotated. The concentration of oxalic acid remaining after irradiation of the solution was determined using potentiometric titration with standardized 0.1-M NaOH. The dose calculation for a decomposition of less than 30% of the initial concentration of oxalic acid was performed using a standard procedure with a

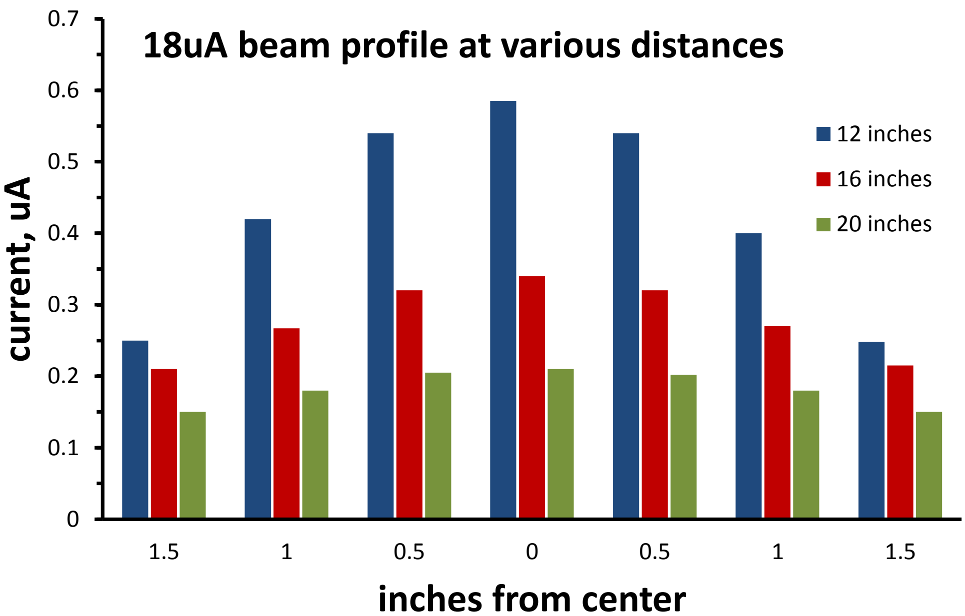

FIGURE 4 Profile of 18-µA Shutter Current Beam at Various Distances

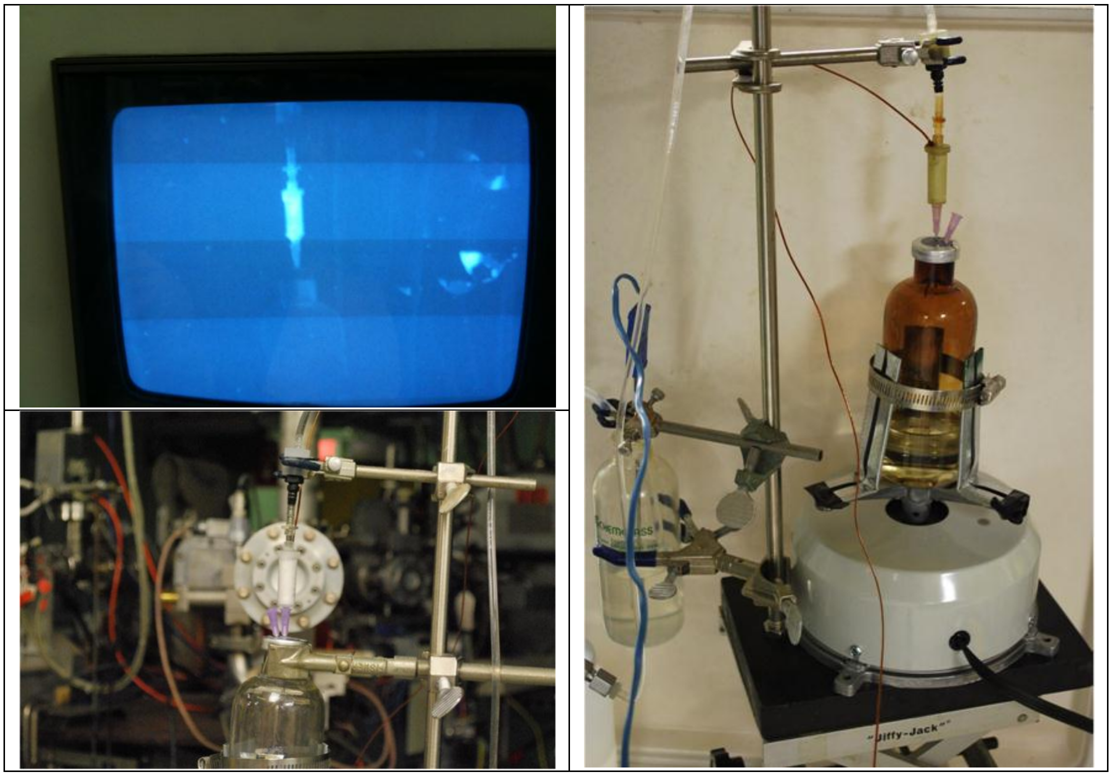

FIGURE 5 Setup for the Irradiation of ABEC Columns (During the irradiation, a solution of 5-M KOH was flowed through the ABEC columns, and the columns were rotated to achieve an even dose rate throughout the column.)

radiochemical yield of G = 4.9 (Draganic 1963). Irrespective of the change in concentration, dose can be calculated with the equation

$$\log D = a \log C + b, \qquad (1)$$

where D is the absorbed dose in eV/mL; C is the number of oxalic acid molecules decomposed in l mL; a = 0.999 and b = 1.344 are constants depending on the initial concentration of oxalic acid (0.6 M) and the number of oxalic acid molecules decomposed. A linear relationship between time (both current and time were monitored) and the dose was obtained and is presented in Figure 6. Based on the data from Figure 6, the dose rate for the irradiation of the ABEC columns with an 18-μA electron beam at 20 in. from the window is 16.851 kGy/min.

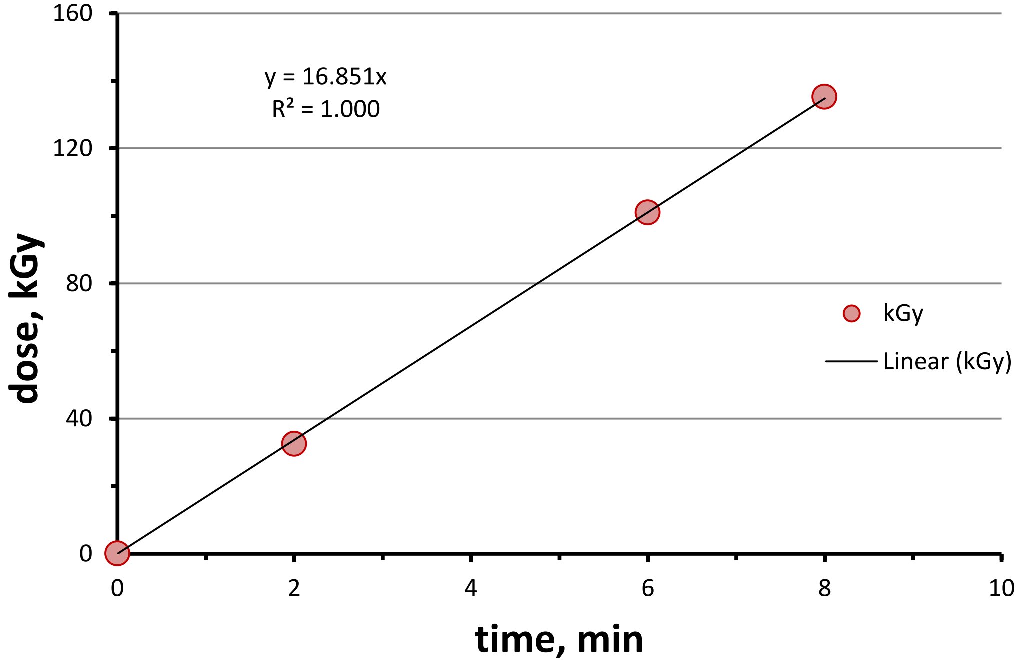

FIGURE 6 Linear Relationship between the Time and Dose Determined from the Irradiations of 1.5 mL of 0.6-M Oxalic Acid at 18-µA Beam at 20 in. from the Window

4 IRRADIATIONS OF THE ABEC COLUMNS

Prior the irradiations, the ABEC columns were rinsed using a 20-mL syringe with the following:

- 10 bed volumes (BV=1.5mL) of 5-M KOH
- 10 bed volumes of deionized water
- 10 bed volumes air push
- repeat 2 times

Seven ABEC columns were irradiated at 5, 10, 20, 50, 100, 200, and 500 kGy using the Van de Graaff generator. It should be noted that a 5-kGy dose represents a dose higher than that calculated by MCNPX for a 20-Ci generator using the same ABEC column for seven consecutive runs (3.5 kGy).

During irradiation, a solution of 5-M KOH was flowed through the ABEC columns at 1 mL/min, and the columns were rotated to achieve an even dose rate throughout each column. It was observed that after exposing the columns to >100 kGy the color of the resin changed from light yellow to darker yellow. In addition, some coloration of the column container was observed for the highest doses. Solutions of 5-M KOH that were used to rinse the ABEC columns prior to (first wash) and during the irradiation were analyzed using FT-IR and UV-Vis spectroscopy for the presence of any constituents of the column that could elute or potentially breakdown during the irradiation. Both FT-IR and UV-Vis spectra of the solutions indicated the presence of species other than 5-M KOH. It was also observed that polyethylene glycol (PEG), which is an active component of the ABEC column, can be dissolved in 5-M KOH, producing a "milky" solution that clears after centrifugation and forms two liquid phases. "Milky" solutions were also observed during rinsing of the ABEC columns prior to the irradiation; they disappeared after repeated washing with 5-M KOH, deionized water, and flushing with air as advised by NorthStar. The FT-IR spectrum of a white solid that was observed in the 5-M KOH after rinsing the columns and before irradiation confirmed that the solid was polyethylene glycol (Figure 7).

The FT-IR and UV-Vis spectra of 5-M KOH solution that was used to rinse the columns during irradiations are shown in Figures 8 and 9. Both UV-Vis and infrared spectroscopy reveal that some components of the column or its degradation products were present in the solution. Irradiated columns were sent to NorthStar to perform Tc sorption efficiency test.

Loading and washing experiments performed by NorthStar on irradiated resins did not show any decrease in recovery of Tc-99m. A slight decrease in Mo recovery was observed for resins irradiated at doses >5 kGy; however, the content of Mo-99 in Tc-99m product was below USP (U.S. Pharmacopeia) specifications for all irradiated resins.

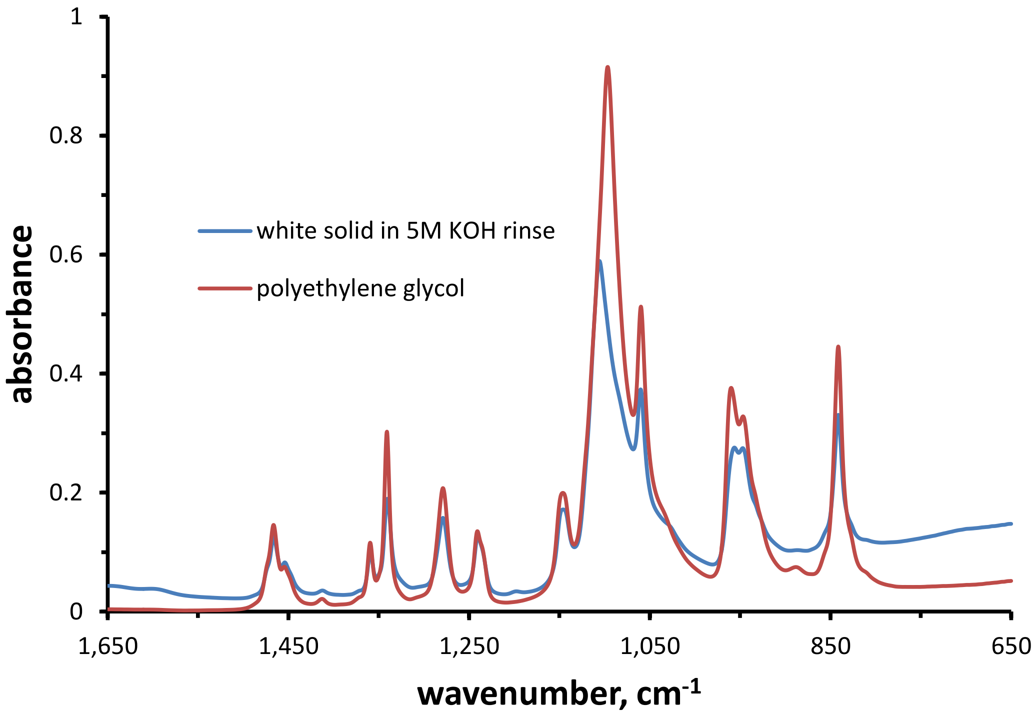

FIGURE 7 FT-IR Spectrum of the White Solid Eluted from the ABEC Column with 5-M KOH Prior to Irradiation, Compared with Spectrum of Solid Polyethylene Glycol Sample

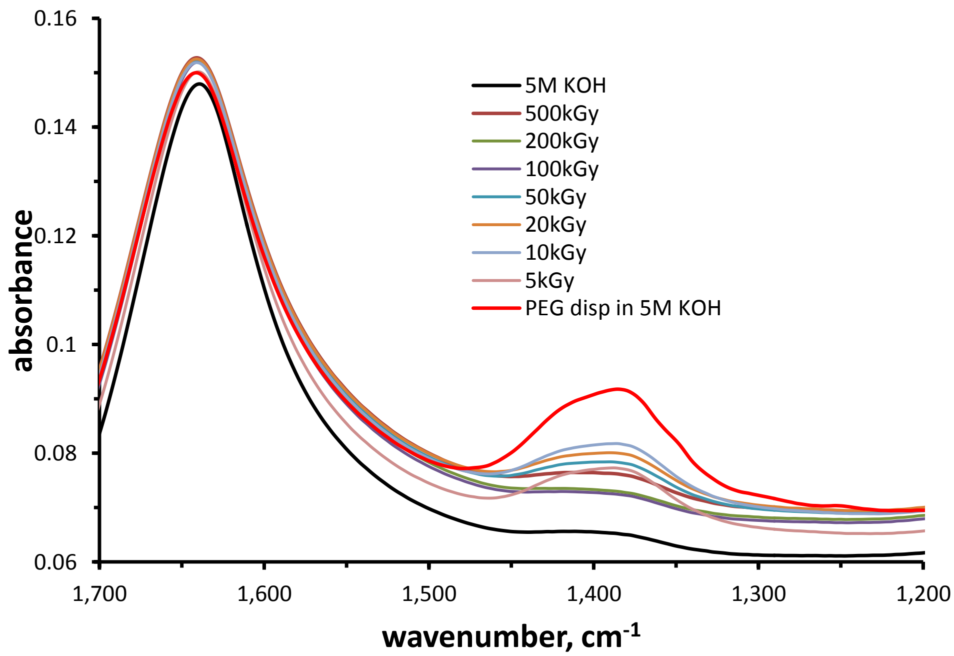

FIGURE 8 FT-IR Spectra of 5-M KOH Solution Used to Rinse Irradiated ABEC Columns at Different Doses, Compared to the Spectrum of PEG Dispersed in 5-M KOH

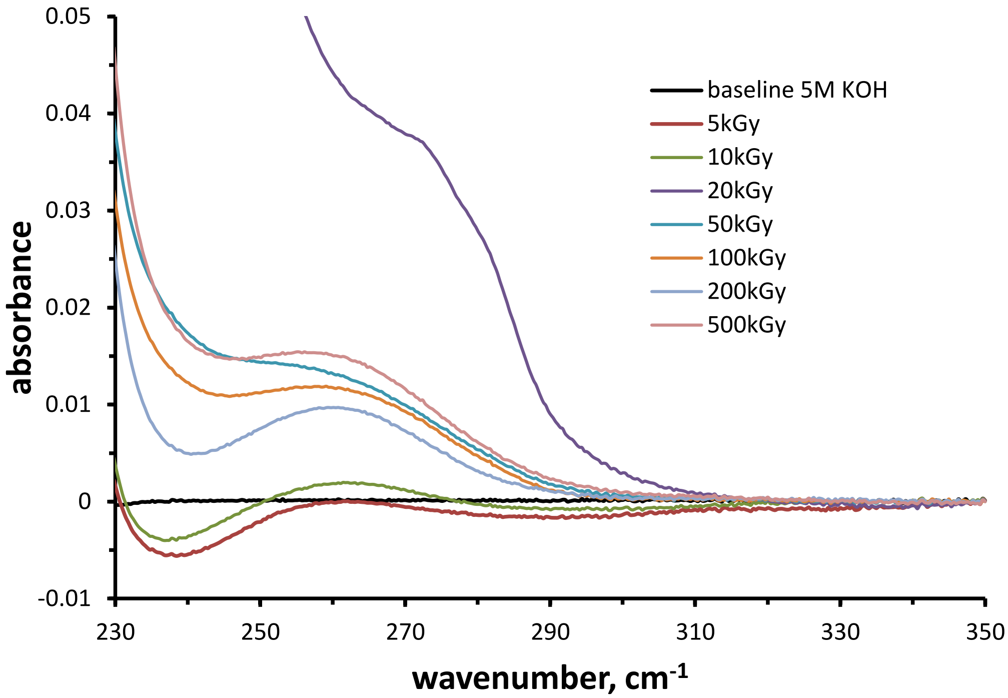

FIGURE 9 UV-Vis Spectra of 5-M KOH Solution Used to Rinse Irradiated ABEC Columns at Different Doses

5 SUMMARY

Monte Carlo calculations have been performed using MCNPX to estimate doses delivered to ABEC columns during seven consecutive loadings of a Mo-99/Tc-99m solution with 20 Ci (on the first day) of Mo-99. Based on the calculations, the total estimated dose absorbed by the resin used for seven consecutive days is ~3.5 kGy. To check radiolytic stability of the resin, seven ABEC columns were irradiated at 5, 10, 20, 50, 100, 200, and 500 kGy using the Van de Graaff generator with continuous flowing of 5-M KOH during the irradiation. It was observed that polyethylene glycol (PEG), which is an active component of the ABEC column, or its degradation products were partially eluting by KOH solution during the irradiation. However, the tests performed by NorthStar on irradiated resins have shown that even significantly higher doses than 3.5 kGy did not affect the recovery of Tc-99m, and the content of Mo-99 in the product vial meets USP specifications.

6 REFERENCE

Draganic, I., 1963, "Oxalic Acid: The Only Aqueous Dosimeter for In-Pile Use," *Nucleonics* 21(2), 33–35.

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