Thermal separation of ^{99m}Tc from Molybdenum targets

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Introduction

Thermal separation is defined as a mass transfer process driven by molecular forces. The process involves the heat transfer between two phases with different composition. In general, thermal separation occurs when heat is generated in the system additionally to the already existing phases. In a second phase the mass is transferred in the system (adsorption) and at the end of this step the separation is completed. The thermal separation can be achieved in temperature or concentration gradient function of system configuration [1]. Thermo-chromatography is a process in which the separation occurs in gaseous phase. By passing a heated gas through a column a thermal gradient is created with a continuously decreasing temperature along the column. The separation occurs based on the different volatilization temperatures, the less volatile species will condense on the column walls at the higher temperatures and the highly volatile compounds will condense at lower temperatures. Parameters like temperature, carrier flow rate, column geometry and length have impact on the absorption of the compound on the column material affecting the separation efficiency. The thermal separation has been used for separation of Molybdenum (Mo) and Technetium (Tc) by either sublimation in the case of ^{94m}Tc {2,3,4} or dry distillation in the case of ^{99m}Tc from neutron irradiated MoO$_3$ [5]. The thermal separation process has been used in the development of a new type of Mo/Tc generators starting from the MoO$_3$ as target material for production of ^{99m}Tc in linear accelerators [6]. Dry distillation has become a standard procedure for separation of radioiodine from tellurium targets [7]. The present paper describes the thermal separation of a three component system (Cu/Mo/Tc) used as a target in the production of ^{99m}Tc through the ^{100}Mo(p,2n) reaction.

Material and Methods

The separation method involves the use of oxygen as a carrier gas and oxidation agent. The method is based on the different volatilization temperatures of Tc formed oxides and the MoO$_3$ formed in the system during the oxidation. In the presence of oxygen the existing Tc is oxidized to its anhydride as Tc$_2$O$_7$ (b.p. 319 ^{o}C; m.p. 110.9 ^{o}C) following the reaction:

$$4Tc + 7O_2 \rightarrow 2Tc_2O_7$$
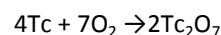
The T$_2$O$_7$ has a saturated vapor pressure of 310 ^{o}C whilst Mo is completely oxidized to MoO$_3$ having a sublimation temperature at 750 ^{o}C. The initial experimental setup comprised a quartz tube (6 mm internal diameter, 40 cm long) which is introduced into a horizontal tube furnace (model 55035A, Lindberg). The left end of the quartz tube is connected to a pure oxygen supply which flows through the separation tube at a rate of 10 mL/min. The other end of the tube is opened to the atmosphere and protected with quartz wool. The quartz tube is heated over a length of 23 cm at a temperature of 850 ^{o}C. The heated carrier gas is flowing on the tube length and the temperature gradient is created along the tube from 850 ^{o}C to room temperature. During the process, the oxygen carries out the Tc oxides to a lower temperature and Tc$_2$O$_7$ is deposited in the cooler region of the tube in a similar manner as described by Tachimory [5]. The temperature gradient is calibrated by measuring the temperature inside the tube at each centimeter along its length (Fig. 1).

FIGURE 1. Experimental system used in the Mo/^{99m}Tc thermal separation experiments

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The radioactivity counting is performed by scanning the tube along its length every 2 centimeters by using a detection system shown in figure 2. The system comprises a GM tube coupled to a computer controlled linear actuator (Velmex Unislide). The tube is placed at a distance of approximately 25 mm from the collimator of GM.

FIGURE 2. Detection system setup used in the Mo/Tc separation

Preliminary testing using Mo powder
Prior to testing the three component separation, a reference test was performed by using 120 mg of natural Mo powder (Alpha Aesar, 99.9 %) soaked with 50 MBq NaTcO$_4$ (Cardinal Health, radiochemical purity >95 %). After evaporation the dried powder was introduced into a quartz tube (6 mm ID, 40 mm long) and heated up to 850 °C in the presence of oxygen flowing at a rate of 10 mL/min.

Three component separation
The targets prepared for the production of ^{99m}Tc by a cyclotron were comprised of copper (Cu) (C101, oxygen free) support having a Mo layer deposited on the surface in an elliptical form as described in literature [8,9]. About 60 to 250 mg of Mo (99.9%, Alpha Aesar) was deposited on the target surface. 70 MBq of Tc (Cardinal Health) as NaTcO$_4$ (> 99 % radiochemical purity) was deposited on the Mo insert to mimic the conditions created during proton irradiation. The Tc spike was evaporated to dryness and the Cu/Mo/Tc target was then introduced into the experimental setup. The process was allowed to continue for 20 min. The experiment was carried out by inserting the target plates in a quartz tube (CanSci, Canada) of similar design to those described by Fonslet for the separation of radio-iodine from TeO$_2$ targets [7]. The quartz tube can be seen in FIG. 2 and illustrated with dimensions indicated in FIG. 3.
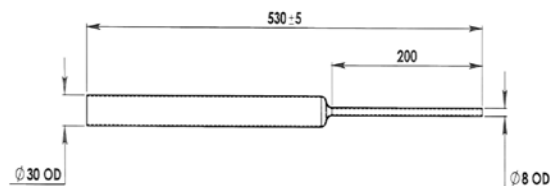

FIGURE 3. Drawing of the quartz tube designed to hold a 55×20 mm target plate.

Separation of in-situ cyclotron produced Tc by irradiation of Mo targets with a proton beam
A third set of experiments have been performed for in-situ generated Tc by irradiation of circular targets containing approximately 60 mg Mo deposited on a copper support. The targets were irradiated for 30 min with a proton beam with the energy of 15 MeV and a current of 50 µA. The separation was performed using similar experimental conditions as previously described. The quartz tube was scanned in length by using a RadioTLC scanning system calibrated for ^{99m}Tc and [99]Mo isotopes.

After the thermal separation was completed ^{99m}Tc was recovered as NaTcO$_4$ by selectively washing the quartz tube with 1 M NaOH (Fisher) solution. The presence of Mo in the NaTcO$_4$ solution was verified by a colorimetric strip test (EM-Quant Mo test kit, Millipore). The presence of copper was qualitatively analyzed by adding a few drops of concentrated NH$_4$OH (Fisher) solution and checking the formation of Schweitzer reagent.

Results
Thermal separation of Tc-Mo powder
After 20 min the deposition of MoO$_3$ was observed as yellow crystals in the region of temperature of 770 °C, which is in accordance with the results reported in the literature [5]. The activity of ^{99m}Tc was detected at about 5 cm from the exit of the tube furnace in a temperature range starting with 310 °C and ending at 46 °C (FIG. 4).

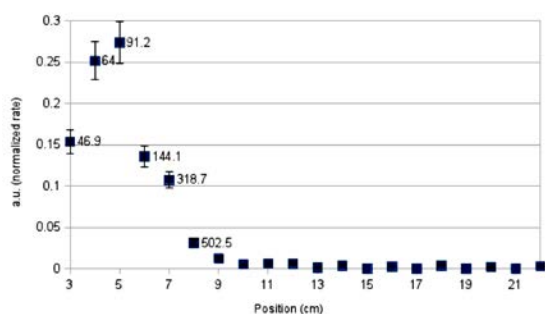[1]Corresponding author, E-mail: lidia.matei@teambest.com

FIGURE 4: Mo powder spiked with ^{99m}Tc: The measured rate along the quartz tube as a function of approximate position along the tube. The temperature of the tube for the points of significant rate above background is labeled to the right of each point in C. The rate is area normalized to 1.

The separation efficiency was greater than 90 %, with most of the radioactivity being recovered in the final solution. The presence of Mo was not detected in the purified solution.

Thermal separation from three component system

The oxidation in a three component system is a competitive reaction between Cu oxides formation and Mo/Tc oxidation. By exposing the plate Mo target in the oxygen flow the oxidation mechanisms involves three steps: adsorption of O_2 molecules onto metallic surface followed by oxidation of metals and then oxide separation based on the volatilization temperatures. The obtained results confirmed the oxidation process of Cu which involves two phases: the partial oxidation with formation of Cu_2O (red) and total oxidation with formation of CuO (black) as described by Zhy [10]. The formation of these two oxides is inhibiting the formation of Tc_2O_7 and its transportation in the cooler regions of the quartz tube hence its condensation in the region of temperatures below 300 °C. At least 50 % of radioactivity has been found on the target insertion point either as Tc_2O_7:MoO_3 mixture or trapped on the disk layers most probably as $Cu(TcO_4)_2$ embedded in the Cu_2O lattice (FIGURE 2). This can be explained by the the formation of Cu_2O in the first oxidation phase which is competing with the oxidation of Mo and Tc. A concurrent reaction with inhibiting effect on the separation process can be the reaction between CuO and MoO_3 with formation of $CuMoO_4$ (yellow-green) at about 500–700 °C [11]. The mechanism is different when the disc targets are used and Tc is generated in situ by proton irradiation. All the oxidation reactions are competitive; the formation of two Cu layers is visible (FIG. 5) but

the Mo and Tc oxides are separated. Mo is deposited on the quartz tube walls and Tc was detected on the cooler region of the tube (FIG. 6).

FIGURE 5. Copper target support after the separation of Mo/Tc generated *in situ* by irradiation of disc Mo targets with 15 MeV proton beam at 50 μA. CuO (black)

FIGURE 6. MoO_3 crystals deposited in a white – yellowish layer on the quartz tube walls

The difference between separation profiles from the two types of targets could be explained by the different conditions applied for oxidation. One reason could be the different Cu:Mo ratio on the plate target 140:1 (w/w) compared with 90:1 (w/w) for disc targets. The oxidation reaction is more competitive in the case of target plates due to a higher content of Cu hence the separation efficiency was lower. A second reason could be the chemical form of Tc in the system during the first phases of oxidation. The target plate was spiked with Tc as pertechnetate in saline solution. During the evaporation a small amount of Cu was partially oxidized. In the partial oxidation step a part of Cu (II) reacted with ionized Tc oxides probably with the formation of $Cu(TcO_4)_2$. The mechanism is different when the Tc is generated *in situ*, the oxidation of Tc with formation of Tc_2O_7 being total and complete leading to a better separation process in the three component system.

Conclusion

The efficiency of the thermal separation of Mo and Tc oxides is higher than 90 % when the process is carried out on Mo powder. In a three component system containing high Cu:Mo ratio such as (140:1 w/w) the separation was inhibited by the competitive reaction. In the case of lower Cu:Mo ratio of 90:1 (w:w) the oxidation process led to a better Mo:Tc separation. After separation, the $NaTcO_4$ solution has been characterized. No traces of Cu or Mo have been

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identified in the final product and the radio-chemical purity of separated NaTcO$_4$ was higher than 95 %.

Further studies will comprise a new approach of using plated copper as target support.

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