Synthesis and Characterization of Molybdenum Phthalocyanine as Target Material for High Specific Activity Molybdenum-99 Production

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Abstract: *High specific activity is a necessity in the fabrication of $^{99}Mo/^{99m}Tc$ radioisotope generators. Recoil reaction with molybdenum phthalocyanine (Mo-Pc) target material is a method that could be used as an alternative method for increasing specific activity in ^{99}Mo production in light of tightening regulation of highly enriched uranium irradiation. Mo-Pc was synthesized via solid-state reaction between ammonium heptamolybdate and phthalonitrile in a reflux system at 300 °C for 3 h. This optimum condition was identified after performing several variations of temperature and time of reaction, considering FTIR spectra, the yield of product and melting point of the product. XRD measurement showed that Mo-Pc synthesized at optimum condition was free from MoO_2, phthalimide and unreacted molybdenum. Mo-Pc has UV-vis properties of Q-band absorption between 600 and 750 nm when dissolved in tetrahydrofuran, dimethylformamide and trifluoroacetic acid. In the preliminary study of irradiation of 1 g Mo-Pc at $3.5x10^{12}$ n cm^{-2} s^{-1} neutron flux, followed by dissolution in tetrahydrofuran and extraction of ^{99}Mo into NaOH, we obtained ^{99}Mo solution with a specific activity of 682.35 mCi/g Mo, this being 254.61 times higher than in the regular MoO_3 target.*

Keywords: *recoil; high specific activity; phthalocyanine; characterization*

■ INTRODUCTION

Successful application of technetium-99m (^{99m}Tc) as the most commonly used medical radioisotope reflects the successful development of radioisotope generators using the fission products of highly enriched uranium (HEU) [1-3]. Users of ^{99m}Tc are highly dependent on ^{99}Mo supply from five main research reactors, and aging and maintenance schedules for these reactors has led some researchers to seek alternative supply routes to secure ^{99m}Tc supply [3-4]. As well as optimizing low-enriched uranium (LEU) as a substitute for HEU, some researchers have revisited the reactor activation route for ^{98}Mo to provide ^{99}Mo.

The main obstacle of this activation route for ^{99}Mo is the low specific activity of ^{99}Mo targets (300–1000 mCi/g) compared to HEU targets (10^4 Ci/g). In order to achieve adequate activation of ^{99}Mo, the amount of molybdenum target must be increased. In contrast, the bound capacity of the most commonly used alumina columns is limited, at only 20 mg Mo/g of alumina, meaning that more alumina and more eluent are needed to separate and elute ^{99m}Tc from ^{99}Mo. Several studies of sorbent materials with higher molybdenum-binding capacity and of other methods of radioisotope generation have been conducted [2,5], but these have yet to be widely used. Other studies have sought to use the ability of recoil reactions to increase the specific activity of neutron-activated ^{99}Mo [6-7].

When a thermal neutron is captured in a target nucleus only thermal energies are involved and these are far from sufficient to cause chemical changes; however, when a gamma ray is emitted from a slow-moving compound nucleus, chemical changes may occur. This

effect (the Szilard-Chalmers effect) can cause persistent chemical changes [8].

When irradiated, Mo atoms undergo transmutation from stable ^{98}Mo isotopes to radioactive ^{99}Mo isotopes. When ^{99}Mo is formed, the Szilard-Chalmers effect occurs as the nuclei achieve an excited state following neutron capture and during radiation of γ-quants, radiating recoil energy of E0~30–100 eV [8]. Recoil energy is much greater than the energy of the chemical bond of the atom in the crystal structure, so the radioactive ^{99}Mo atoms will be freed from the initial molybdenum compound structure, but stable ^{98}Mo will remain as the initial compound. One of the likely compounds in which recoil reactions could take place is phthalocyanine.

Fig. 1 shows the Mo-Pc structure in which phthalocyanine is a ring structure built of four isoindole units. Each isoindole is connected to each other by an N-aza atom. A metal atom, in this case, molybdenum, usually exists in the center of phthalocyanine and is connected to the ring via four Mo-N bonds. The Mo-N bond could be broken by recoil energy in the Szilard-Chalmers reaction and Mo-Pc could be synthesized in a number of ways, either with or without solvent. Precursor o-cyanobenzamide, diamino phthalimide or phthalic acid could be used for phthalocyanine synthesis but this process would require the presence of a solvent. In contrast, phthalocyanine could be synthesized without solvent in ring formation by heating phthalonitrile and ammonium heptamolybdate.

Some studies of phthalocyanine compounds and their characteristics have been carried out, but none of them

have explained Mo-Pc characteristics, thus in this study synthesis of Mo-Pc and its characterization has been carried out. The purpose is to identify the optimum condition for Mo-Pc synthesis and to identify important characteristics of Mo-Pc, such as FTIR spectra, crystallography by XRD, solubility in various solvents and UV-vis absorbance in those solvents. These Mo-Pc characteristics would be basic information for use in future studies of irradiation of Mo-Pc and separation of ^{99}Mo from irradiated Mo-Pc.

■ EXPERIMENTAL SECTION

Materials

Ammonium heptamolybdate p.a. $((NH_4)_6Mo_7O_{24} \cdot 4H_2O)$, phthalonitrile p.a. $(C_6H_4N_2)$, sulphuric acid 98%, dimethylformamide p.a. (DMF), tetrahydrofuran p.a. (THF), trifluoroacetic acid p.a. (TFA), and absolute ethanol were purchased from Merck Millipore. NaOH 0.5 M, TGA solution 10% and potassium thiocyanate (KSCN) solution 10% were prepared by dissolution in distilled water. Whatman filter paper no.1 was used in the filtration process.

Instrumentation

The following equipment was used in this research: reflux system, heating mantle, magnetic stirrer, fume hood, balance (Mettler Toledo, five digits) UV-vis spectrophotometer (Hitachi), quartz cuvette (Q Analytics), XRD (PANalytical X'Pert 3), FTIR spectrometer (Shimadzu) and melting point apparatus (Fischer Scientific).

Procedure

Mo-Pc was prepared by solid-state reaction between ammonium heptamolybdate $((NH_4)_6Mo_7O_{24} \cdot 4H_2O)$ and phthalonitrile $(C_6H_4(CN)_2,$ Merck). The molar composition ratio between molybdenum and phthalonitrile was 1:4, at 1.765 g and 5.125 g respectively. The reaction was carried out in a ventilated reflux system in a round flask equipped with a quicksilver thermometer and condenser and heated using a heating mantle.
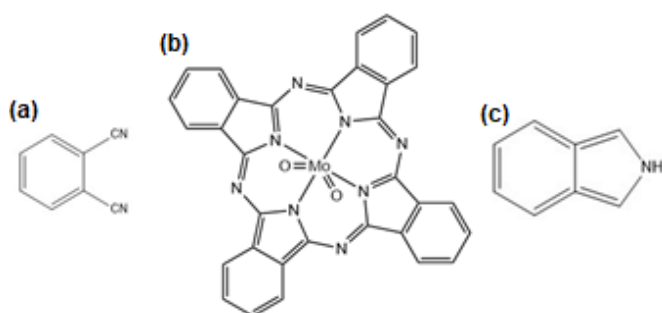
Fig 1. Compound structures: (a) phthalonitrile; (b) molybdenum phthalocyanine; (c) isoindole

Optimization of temperature and time of reaction

Optimization of the reaction was carried out by varying temperature and time of reaction. Based on Wolfram's phthalocyanine synthesis condition [9] (300 °C, 3 h), reaction temperatures were varied at 275, 300, and 325 °C for 3 h, and time of reaction was varied at 60, 120, 180, and 240 min after the optimum temperature was obtained.

Purification of Mo-Pc

Purification was carried out by washing the solid formed with hot water containing 1 M potassium hydroxide, to remove any unreacted molybdenum. Then ethanol and acetone were used to remove unreacted phthalonitrile and phthalimide until the washings were colorless [9-10]. Using a few drops of filtrate as the sample, several spot tests for molybdenum were conducted with TGA 10%, concentrated HCl and KSCN 10%. Orange color in the spot test indicated a positive result for molybdenum content. Mo-Pc solid was washed with water until spot-test results were colorless. Mo-Pc solid was dried in an oven at 40 °C for 4 h and weighed and re-dried in a desiccator until its weight was constant.

Characterization of synthesis products

Melting points of the compounds were measured using Fischer Scientific melting point apparatus. FTIR spectra of the compounds were recorded by Shimadzu FTIR using the transmission technique, by creating Mo-Pc in KBr pellets. XRD patterns of solids were recorded by PANalytical X'Pert Pro XRD. UV-vis spectrophotometric method using a Hitachi spectrophotometer was applied to determine molybdenum content in solution [11]. FTIR and XRD setup parameters are shown in Table 1.

V-vis absorption properties of Mo-Pc

Saturated solutions of Mo-Pc were prepared by dissolving an amount of Mo-Pc in selected solvents until precipitation occurred. Selection of solvent (sulphuric acid 98%, DMF, THF, and TFA) was based on a previous study [12]. Dissolution was carried out by shaking and stirring at room temperature, but with the use of an ice bath for dissolution with sulphuric acid. Supernatant and precipitation of undissolved Mo-Pc were separated by

Table 1. Setup parameters of FTIR and XRD measurement

FTIR properties (Shimadzu)	
Scan range (cm^{-1})	4500–500
Resolution (cm^{-1})	4
Number of data points	8192
Number of scans	64
XRD properties (X'Pert Pro)	
λ of the X-ray source	1.540598 Å (Cu Kα)
Scan range (2θ)	5 to 90°
Step angle	0.01°
Time of step	1 sec
Detector	PW3011 (sealed proportional gas)

centrifugation and the supernatant was measured using a UV-vis spectrophotometer.

A preliminary study of Mo-Pc irradiation

One gram of synthesized Mo-Pc at optimized condition was weighed and transferred into a quartz ampoule and sealed by glass welding. Ampoules were packed into capped aluminum capsules before being inserted into irradiation position at the TRIGA 2000 research reactor, Bandung. Mo-Pc was irradiated for 72 h with 3.63×10^{12} n cm^{-2} s^{-1} neutron flux. At the end of irradiation, the target was cooled for 48 h then transferred into a radioisotope processing box shielded with lead. Irradiated Mo-Pc was dissolved in 50 mL tetrahydrofuran and stirred at room temperature for 3 h. The Mo-Pc suspension was then filtered through Whatman no. 1 filter paper. Radioactivity of Mo-99 in the filtrate and sediment was measured using a dose calibrator.

Mo-99 in THF medium in the filtrate was extracted into 3 M NaOH and its radioactivity in the NaOH medium was measured by dose calibrator. Mo-99 radioisotope solution was then allowed to decay for 1 month prior to molybdenum content determination by the spectrophotometric method.

■ RESULTS AND DISCUSSION

Molybdenum phthalocyanine can be prepared by several reactions, mainly solvent reactions [9-11], solventless reactions or solid-state reactions [9]. By

using o-phthalonitrile instead of its dinitrile precursor [12], the synthesis pathway could be simplified by using just two reactants.

When two solid reagents were heated, phthalonitrile melted at around 140 °C. At 200 °C, a brown liquid formed and this was followed by vigorous gas evolution at 240 °C, so the reaction must be performed in an open reflux system. This gas evolution may have occurred because the reaction between molybdenum and phthalonitrile had started, giving NH_3 gas as a by-product:

$$(NH_4)_6Mo_7O_{24} \cdot 4H_2O + 28\ C_8H_4N_2 \rightarrow \\ 7\ C_{32}H_{16}N_8MoO_2 + 6\ NH_3 + 7\ H_2O \quad (1)$$
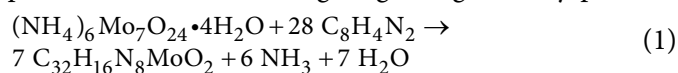
The reason for using ammonium heptamolybdate instead of molybdenum trioxide is that molybdenum (VI) could be reduced to Mo (V) by the formation of ammonia, but there was no synthesis reaction of Mo-Pc when molybdenum trioxide replaced ammonium heptamolybdate. Temperature and time of reaction were varied to find the optimum reaction condition.

Optimization of Temperature and Time of Reaction

Optimization was investigated at three different temperatures. The results, as presented in Table 2, show that heating at 275 °C gave a brighter color of synthesis product compared to heating at 300 and 325 °C. Lower

reaction temperature resulted in a brighter greyish-blue solid and a lower yield of product compared to higher reaction temperature. Higher temperature gives more kinetic energy, enabling reactants to undergo complete reaction. Melting point test results showed that all products in the temperature variations were different from the initial melting point of the reagent (phthalonitrile and ammonium heptamolybdate). All products sublimated at 380–400 °C to a bright violet product. The FTIR peak list presented in Table 3 shows that the product at 300 °C has similar spectral characteristics to zinc phthalocyanine (Zn-Pc) as a reference spectrum. The peaks at 891 and 968 cm^{-1} were the signals for Mo-N and Mo=O bonds respectively, whereas the peaks at 950 and 881 cm^{-1} indicated that Zn=O and Zn-N bonds in Zn-Pc existed. By Hooke's law calculation, we can conclude that vibration frequency (v) of Zn=O or Zn-N is lower than Mo=O and Mo-N because Zn has a lower reduction mass than Mo.

Those peaks do not appear completely in the 275 and 325 °C products. In the 275 °C product, the Mo-N peak appeared but Mo=O did not. In contrast to the 275 °C product, Mo=O peak appeared at 325 °C but Mo-N did not. According to Achar [13], after being heated from 500 to 1000 °C, Cu-N bonds in Cu-phthalocyanine

Table 2. Reaction temperature optimization in molybdenum phthalocyanine synthesis

Reaction temp. (°C)	Synthesis product	Melting point (°C)	Yield (3 replicates)
275	Greyish-blue solid	Sublimated at 380	69.08±6.99%
300	Bluish-violet solid	Sublimated at 400	82.35±2.25%
325	Dark bluish-violet solid	Sublimated at 400	84.45±2.52%

Table 3. Peaks in FTIR analysis of synthesis products (temperature variation)

Mo-Pc (cm^{-1}, 275 °C)	Mo-Pc (cm^{-1}, 300 °C)	Mo-Pc (cm^{-1}, 325 °C)	Zn-Pc (cm^{-1}, standard)
725	725	725	723
748	777	779	775
N/A	841	839	N/A
889	891	N/A	881
941	N/A	N/A	N/A
N/A	968	968	951
N/A	1117	N/A	1117
1188	1159	1159	1165
1284	1286	1284	1283
1329	1329	1329	1331

polymer are degraded. Thus, Mo-N peak appeared at the lower synthesis temperature and degraded at the higher synthesis temperature. Mo=O bond was formed as an oxidation product of Mo. Despite having the highest yield, the 325 °C product does not have an IR peak from the Mo=N bond. Based on the FTIR results presented in Table 3, 300 °C was considered as the optimum temperature for Mo-Pc synthesis.

Optimization of reaction time was carried out at a reaction temperature of 300 °C with a time of reaction being measured from the commencement of heating. From the results of reaction-time optimization presented in Table 4, it can be seen that 180 min gave a higher product yield than 240 min of reaction. It is assumed that some of the product might have sublimated or been destroyed by longer heating time, but this must be proved by supporting references and further analysis. All product did not undergo melting but sublimated at temperatures above 380 °C.

The product at 180 min has the most complete IR peak. Mo=O and Mo-N peaks at 970 and 891 cm^{-1}, respectively, did not appear in the 60- and 120-min spectra, possibly because there was not enough time to establish complete Mo=O and Mo-N bonds in the phthalocyanine core. The 240-min product has the same IR peak pattern as the 180-min product (Fig. 2) but the yield of the 240-min product was slightly lower. In consideration of the shorter time giving equal product properties, 180 min was selected as the reaction time for the Mo-Pc synthesis procedure.

XRD Characteristics of Mo-Pc

The XRD pattern of Mo-Pc synthetized in optimum conditions (Fig. 3) showed strong diffraction lines at the following values of 2θ: 7.16, 9.42, 10.82, 12.28, 18.88, 23.84, 26.38, and 28.18°, matching with the following diffraction lines from Wolfram's phthalocyanine [8]: 7, 9, 10.5, 12.5, 18.9, 23.6, 26, and 28°.

Table 4. Reaction-time optimization in molybdenum phthalocyanine synthesis

Reaction time (min)	Synthesis product	Melting point (°C)	Yield (3 replicates)
60	Grey solid	Sublimated at ~380	73.03±1.43%
120	Bluish-violet solid	Sublimated at ~380	82.31±1.31%
180	Dark bluish-violet solid	Sublimated at ~400	84.45±1.24%
240	Dark bluish-violet solid	Sublimated at ~400	83.68±1.88%
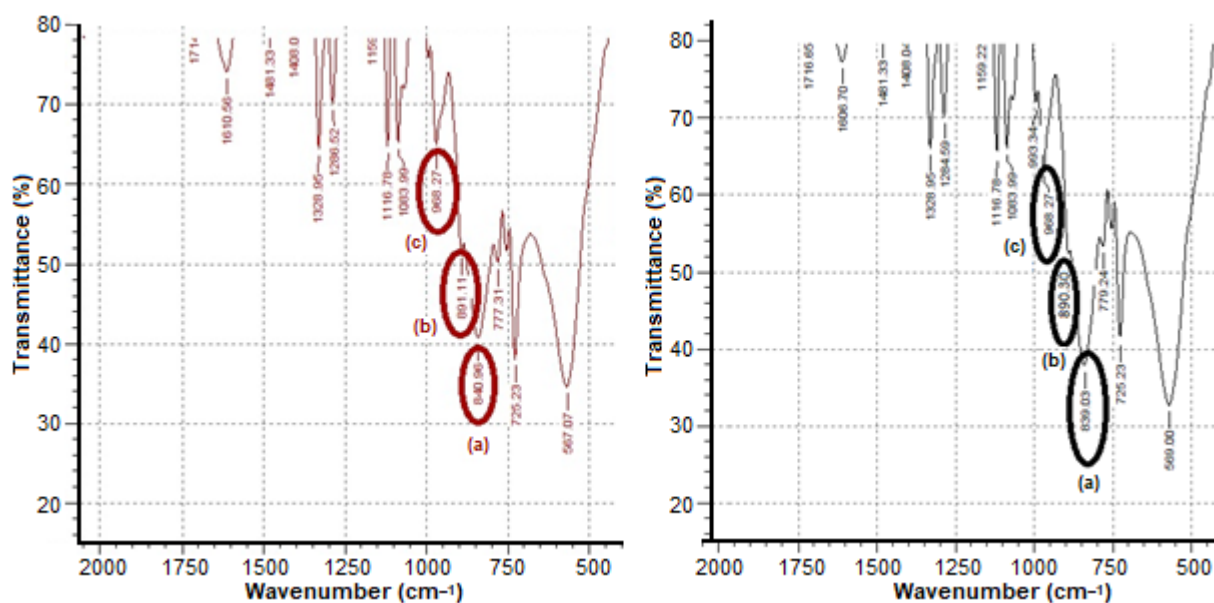
Fig 2. FTIR spectra of Mo-Pc, synthesis temperature 300 °C, time of reaction 180 min (left) and 240 min (right), showing main peaks of Mo-Pc (a) N-isoindole (b) Mo-N vibration (c) Mo=O stretching
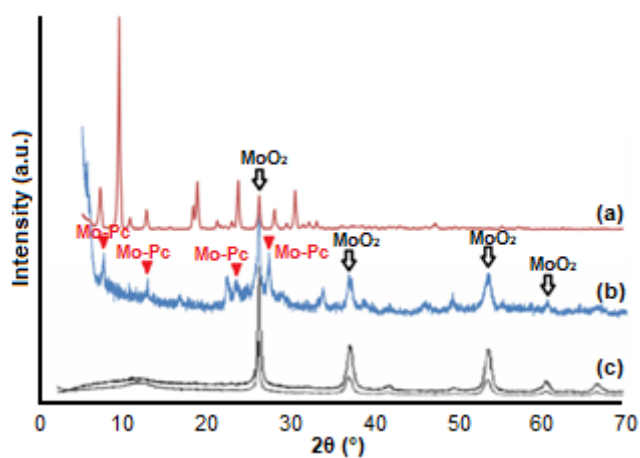
This pattern was in agreement with the pattern for tungsten phthalocyanine [9] with some shift due to the difference in the metal core. Lines due to free Mo [13] and phthalonitrile [14] were absent from this Mo-Pc pattern.

Fig. 4 presents the diffractogram of Mo-Pc synthesized in conditions of non-stoichiometric molybdenum and phthalonitrile. Excess molybdenum was added in this synthesis. This pattern distinctively differs from Mo-Pc synthetized in optimum condition. We compared this pattern with other patterns of MoO_2 [14-15]. Based on the results of these other studies, MoO_2 peaks are identified in Fig. 4. These peaks were fused with Mo-Pc peaks. It can be concluded that two forms of molybdenum existed when excess molybdenum was added into the reaction: Mo-Pc and MoO_2.

Some diffraction lines at the following values of 2θ: 7.16, 12.28, 23.84, 26.38, and 28.18° matched diffraction lines for Mo-Pc, whereas the diffraction lines at 26.38, 36.84, 53.42, and 60.66° match with diffraction lines from MoO_2. Lines due to free Mo [16] and phthalonitrile [17] were absent from this Mo-Pc pattern.
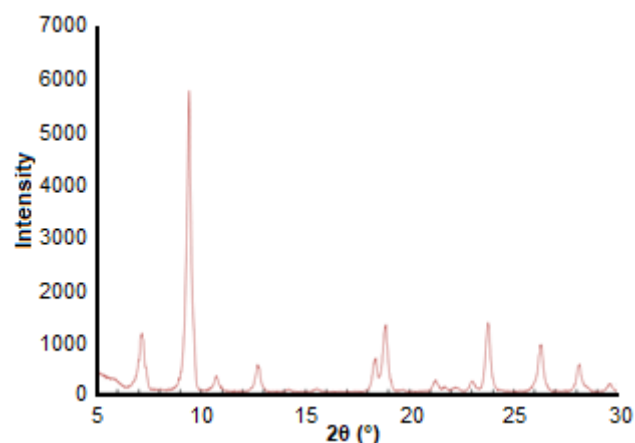
UV-vis Properties of Molybdenum Phthalocyanine

UV-vis spectrophotometer measurement was carried out in different solutions of Mo-Pc. Measurement of Mo-Pc in H_2SO_4 solution was absent due to a strong chemical/solvatochromic effect. Fig. 5 shows the absorption spectra of Mo-Pc in DMF, TFA, and THF.
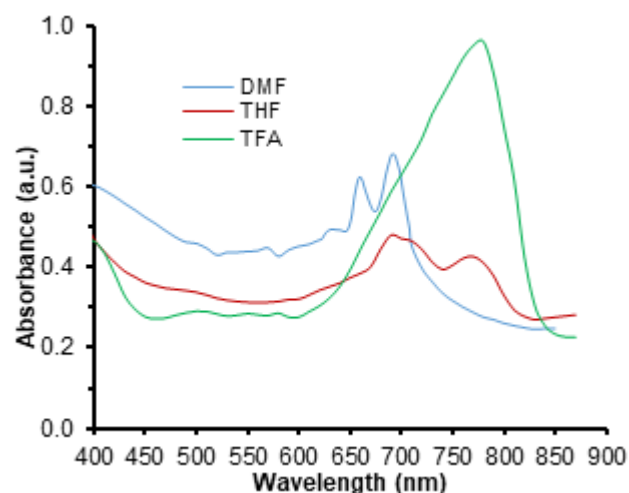
The UV-vis peak of metal phthalocyanine is mainly caused by π-$\pi^{\star}$ electronic transition. This transition is usually known as Q-band transition and results in peaks in the visible region between 600 and 750 nm [12]. In this study, Q-band peak appeared as a split absorption band when Mo-Pc was dissolved in THF and DMF. This splitting was due to protonation of Mo-Pc in THF and DMF [12,18]. Splitting was absent when Mo-Pc was dissolved in TFA. Mo-Pc solution was relatively stable for 3 days with no significant changes in absorption value in the Q-band. Mo-Pc did not show charge transfer between metal (Mo) and phthalocyanine rings, whereas other phthalocyanine compounds such as Mn-Pc and Fe-Pc are

Fig 3. XRD diffractogram of Mo-Pc in optimum condition

Fig 4. XRD pattern comparison between (a) Mo-Pc in optimized synthesis condition (b) Mo-Pc with excess molybdenum and (c) MoO_2 solid [14]

Fig 5. UV-vis spectra of Mo-Pc in three different solvents

Table 5. Molybdenum content and specific activity of ^{99}Mo

Target type	Activity (mCi) after 5 days cooling*	Mo content in solution (g)	Specific activity	Enrichment factor
MoO$_3$ (225 mg)	0.40	1.5×10^{-1}	2.68 mCi/g Mo	-
Mo-Pc (1 g)	0.58	8.5×10^{-4}	682.35 mCi/g Mo	254.61

well known for their charge transfer and are very unstable in solution form [19-20].

A Preliminary Study of Mo-Pc Irradiation

Irradiation of 1 g Mo-Pc resulted in 0.58 mCi of ^{99}Mo in the Mo-Pc target after 5 days of irradiation. We also irradiated natural MoO$_3$ as a control to be compared with Mo-Pc irradiation. According to molar calculation, 1 g of Mo-Pc contains about 150 mg of elemental Mo, thus 225 mg of MoO$_3$ is equivalent to the content of Mo in 1 g of Mo-Pc. The yield of irradiation was about 96.3% from the calculated activity. After several dissolutions with THF and extraction processes into 3 M NaOH, 89% ^{99}Mo remained in the final solution. This yield was far better than other reported results using different types of molybdenum molecules [21-22].

Table 5 indicates that 0.85 mg of Mo was found in the solution by spectrophotometric determination of Mo content [23]. This Mo content was 0.56% compared to initial Mo content in 1 g of irradiated Mo-Pc (150 mg). Most of the molybdenum remained in Mo-Pc structure and was not extracted into NaOH during the Szilard-Chalmers reaction, indicating that the specific activity of Mo-99 solution could, therefore, be increased.

This preliminary study shows that Mo-Pc irradiation followed by several dissolutions and extraction processes exhibits enrichment in ^{99}Mo specific activity. The specific activity could be increased by utilization of Mo-Pc, at 254.61 times higher than irradiation of natural molybdenum oxide. This enrichment factor was equal to that found in one study [22] but slightly less than in another study [21]. However, both of these previously reported results had lower yield compared to Mo-Pc utilization for Mo-99 production as investigated in this study.

Further investigation will be carried out to optimize the production of ^{99}Mo by Szilard-Chalmers reaction.

■ **CONCLUSION**

Mo-Pc was successfully synthesized with an optimum temperature of synthesis of 300 °C and 3 h of reflux. Mo-Pc was sublimated at 400 °C without undergoing melting when measured with melting point apparatus. FTIR measurement showed characteristic peaks of Mo-N and Mo=O at 891 and 968 cm^{-1} respectively. XRD measurement confirmed that there was no MoO$_2$ in Mo-Pc synthesized at optimum condition. UV-vis absorption spectra of Mo-Pc solution in THF, DMF, and TFA showed Q-band absorption characteristics between 600 and 750 nm. Protonation of Mo-Pc occurred when Mo-Pc was dissolved in THF and DMF, marked by splitting of the absorption peak. This melting point, FTIR and XRD characteristics could be used as purity criteria when performing Mo-Pc synthesis. A preliminary study of Mo-Pc irradiation showed a specific activity of ^{99}Mo could be increased 254.61 times by utilization of Mo-Pc compared to irradiation of natural molybdenum oxide.

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