

SPECTROPHOTOMETRIC DETERMINATION OF MOLYBDENUM CONTENT IN ^{99m}Tc SOLUTION VIA Mo-TGA-KSCN COMPLEXES FORMATION

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ABSTRACT

SPECTROPHOTOMETRIC DETERMINATION OF MOLYBDENUM CONTENT IN ^{99m}Tc SOLUTION VIA Mo-TGA-KSCN COMPLEXES FORMATION. Quality of Technetium-99m solution is determined from its radiochemical, radionuclidic and chemical purity. One of the major concern about chemical purity of Tc-99m from irradiated natural molybdenum is its molybdenum content or Mo breakthrough. Spectrophotometric method is one of method that could be applied for Mo determination in Tc-99m solution. Molybdenum (V) could form a colored complexes with potassium thiocyanate (KSCN) but Molybdenum (VI) must be reduced before formed a complexes with KSCN. Thioglycolic Acid (TGA) was used as reducing agent to obtain reduced Mo (Mo(V)). A series of optimization process was carried out to find optimum condition of complex formation for analysis purposes. Optimized condition were 3 mL of 25% HCl was added into a volume of Mo sample, followed by 200 μ L of 10% TGA, 1 mL of 10% KSCN, and water addition up to 10 mL total volume. The method is linear over 2 ppm to 30 ppm Mo with regression coefficient 0.9988 ± 0.0007 . The detection limit was 0.212 ppm Mo. Color of the complex has a stability of absorbance up to 120 minutes while stored at room temperature. No significant deviation occurred when 1000 ppm of oxalic acid, methyl ethyl ketone and iron added into sample solution. This complexing method is suitable for spectrophotometric determination of molybdenum content in Tc-99m solution as a part of quality control process.

Keywords: Technetium-99m, Mo breakthrough, activation, complexes, spectrophotometric

ABSTRAK

PENENTUAN KANDUNGAN MOLIBDENUM DALAM LARUTAN ^{99m}Tc DENGAN SPEKTROFOTOMETRI MELALUI PEMBENTUKAN KOMPLEKS Mo-TGA-KSCN. Kualitas dari sediaan teknesium-99m ditentukan dari kemurnian radiokimia, radionuklida dan kimianya. Salah satu masalah terkait kemurnian kimia dari Tc-99m hasil iradiasi molibdenum alam adalah kandungan molibdenumnya atau molibdenum lolos. Metode spektrofotometri adalah salah satu metode yang dapat digunakan untuk menentukan Mo dalam larutan Tc-99m. Molibdenum (V) dapat membentuk kompleks berwarna dengan kalium tiosianat (KSCN) namun molibdenum (VI) harus direduksi terlebih dahulu sebelum membentuk kompleks dengan KSCN. Asam tioglikolat (TGA) digunakan sebagai reduktor untuk memperoleh Mo tereduksi (Mo(V)). Suatu seri optimasi telah dilakukan untuk menentukan kondisi optimum pembentukan kompleks untuk tujuan analisis. Kondisi optimum itu adalah penambahan 3 mL HCl 25% terhadap sejumlah volume sampel Mo dilanjutkan dengan 200 μ L TGA 10%, 1 mL KSCN 10% dan penambahan air sampai tanda batas 10 mL. Metode ini linear dari 2 ppm sampai 30 ppm Mo dengan koefisien regresi 0.9988 ± 0.0007 . Limit deteksi metode sebesar 0.212 ppm. Warna kompleks cenderung stabil selama 120 menit pada temperatur ruang. Penyimpangan berlebih tidak terdeteksi saat 1000 ppm asam oksalat, metil etil keton dan besi ditambahkan ke dalam larutan sampel. Metode pengompleksan ini dapat digunakan untuk penentuan kandungan molibdenum dalam larutan Tc-99m sebagai bagian dari kontrol kualitas.

Kata kunci: Teknesium-99m, lolosan Mo, aktivasi, kompleks, spektrofotometri.

1. INTRODUCTION

Technetium-99m (^{99m}Tc) as the most used radioisotopes in health is produced in BATAN Bandung by extraction method to separate ^{99m}Tc as a daughter of molybdenum-99 (^{99}Mo). This separation method is quite simple but need high personnel competency to separate two fractions of ^{99m}Tc and ^{99}Mo (1).

An important step in ^{99m}Tc production using extraction method is quality control of ^{99m}Tc solution. ^{99}Mo breakthrough level is one of important parameters that must be determined (2). Along with ^{99}Mo breakthrough quantitative assessment, non-radioactive molybdenum breakthrough is determined by semi quantitative spot test methods, while another work was carried out by the determination of molybdenum using molybdenum kits (3). In order to improve the quality of ^{99m}Tc solution, exact quantitative determination of molybdenum must be carried out in quality control procedure of ^{99m}Tc solution.

Spectrophotometric or colorimetric technique is the recommended method in molybdenum determination for radioactive samples despite of more sensitive technique like AAS. AAS method is not recommended for determination of molybdenum in radioactive samples because of burning activities that could lead to air contamination, so a glove box must be used to shield the AAS devices in order to prevent radioactive contamination to environment (4). There are two recommended methods in

spectrophotometric technique for determination of molybdenum : dithiol methods and thiocyanate method (5). Thiocyanate method was selected method for spot test of ^{99m}Tc solution in BATAN Bandung because of its selectivity and sensitivity is higher than dithiol method (5).

The major shortcomings in thiocyanate method is the stability of Mo-Thiocyanate (Mo-SCN) complexes. In spot test using tin oxide as reducing agent, the orange color of Mo-SCN complexes was faded rapidly in order of minutes. Another study employed ascorbic acid as reducing agent but must be coupled with o-phenanthroline to increase stability of the complexes (6). Stability the color of complexes is one of uncertainty factor in analysis using spectrophotometric technique that must be suppressed. Reducing agent plays important role in stability of Mo-SCN complexes because Mo-SCN complexes is stable only in Mo(V) form.

Thioglycolic acid (TGA) was considered as selected reducing agent to replaced tin oxide because of some its excellences. TGA is a selective and sensitive ligand for Molybdenum, Iron, Tin and Silver determination (7).

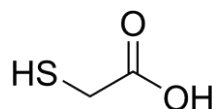


Figure 1. Structure of thioglycolic acid (4)

TGA could act as masking agent to iron by prevent Fe-SCN complexes formation which could interfere Mo-SCN complexes absorbance (7). -SH group in TGA acts as both reducing agent and electron donor for complexes formation. -OH group in acetic acid side acts as electron for complexes formation, as the result, TGA works as reducing and chelating agent (**Figure 1**).

Reduction of molybdenum by TGA could be controlled between Mo(V) and Mo(IV) with Mo(V) as most stable reduction product between both reduction product. By TGA, over reduction of Mo(VI) to lower oxidation number could be avoided (5).

In order to find optimum condition of Mo-SCN complexes formation for analysis purpose, this paper would describe optimization study of Mo(VI) reduction and Mo-SCN complexes formation. Spectrophotometric determination of molybdenum content in ^{99m}Tc solution sample would be carried out by the optimized reagent composition and condition.

2. MATERIAL AND METHODS

Apparatus

Hitachi 12-120 double beam UV-Visible Spectrophotometer with tungsten and deuterium lamp, range 190 nm – 370 nm (UV) 370 nm – 820 nm (visible). Resolution of wavelength selector is 0.1 nm.

Electrophoresis chamber made from polyethylene with electrolyte capacity up to 2000 mL. Length of electrophoresis paper is 14 cm for each pole direction. This electrophoresis chamber was connected

with indigenous DC variable power supply with voltage range 10 – 500 Volt with current limiter at 25 Ampere. Principally, electrophoresis procedure of ⁹⁹Mo was same with other radioisotopes electrophoresis procedure stated in previous study [7].

Single channel analyzer with NaI(Tl) detector was used for electrophoresis paper counting process. Each electrophoresis paper to be counted were cut per 1 cm and inserted into counting chamber. Time for each counting was 4 seconds.

Molybdenum Complexes Formation

200 μ L of 1000 ppm Mo stock solution was added into 10 mL flask. 25% HCl was added into Mo solution prior to thioglycolic acid (TGA) addition. KSCN was added then orange complexes solution was formed. H₂O was added until 10 mL. Volume of HCl, TGA and KSCN were determined in reagent optimization.

Optimization Studies

Thioglycolic Acid works as reducing agent in acid condition. To determine the effect of acid added, the series of 4N HCl, HNO₃ and 2N H₂SO₄ was added into 10 mL flask contain 20 ppm Mo, then 200 μ L of 10% TGA was added followed by 1000 μ L addition of 10% KSCN. Effect of acidity level was investigated by adding various volume of optimized acid.

To determine optimum quantity of thioglycolic acid and KSCN addition, optimization was carried out by varying volume of TGA and KSCN. 50, 100, 200, 300 and 400 μ L of 10% TGA was added into 5 volumetric flasks, each flask contain 20

ppm Mo and HCl. 0, 250, 500, 750, 1000, 1500 and 1700 μL of 10% KSCN was added into 7 volumetric flasks, each flask contain 20 ppm Mo, volume of optimized HCl and volume of optimized TGA. Finally, aquadest was added until 10 mL mark.

All of samples and blanks were measured in Hitachi double UV-Vis Spectrophotometer using identical quartz glass cuvette.

^{99m}Tc Samples Solution

Proses $^{99m}\text{TcO}_4^-$ sample solution was prepared by extraction methods and electrodeposition method. 10 grams of irradiated ^{99}Mo was dissolved in 20 mL 5N NaOH in erlenmeyer flask. 7 mL of Methyl Ethyl Ketone (MEK) was added into the flask and then shaken using automatic shaker for 10 minutes under lead gloves box protection. MEK phase was separated from aqueous phase using separatory funnel. MEK phase containing ^{99m}Tc was dried in water bath for 10 minutes. Finally 2 mL of 0,9% NaCl was added into dried MEK. Procedure of electrodeposition method for separation of ^{99m}Tc from ^{99}Mo was described in previous study (8).

After decayed for 2 days, 1 mL of ^{99m}Tc samples was transferred into 10 mL flask. Volume of optimized HCl was added prior to TGA. KSCN was added at last. Finally H_2O addition was carried out until 10 mL mark. Samples were measured in Hitachi UV-Vis spectrophotometer in maximum wavelength.

3. RESULT AND DISCUSSION

Molybdenum Complexes Formation

The quality control process of ^{99m}Tc produced in TRIGA Bandung Research Reactor consists of some quality test in radiochemical purity, radionuclidic purity, radioactive ^{99}Mo content and non radioactive molybdenum content. Previously, semi-quantitative non radioactive molybdenum content was employed by spot test using thiocyanate method. Previous reducing agent in thiocyanate method was stannous chloride. In order to increase accuracy and sensitivity of quality test for ^{99m}Tc radioisotope solution, spectrophotometric determination of molybdenum was developed.

Thioglycolic acid was studied both as reducing agent or complexing agent for some metals (9). Complexes of Mo-TGA gave yellow colored with absorbance at 370 nm when the blank has no significant absorbance (Figure 2). This result was in accordance with other result (10). Absorbance of the Mo-TGA complexes was depended on the pH of the solution. In the

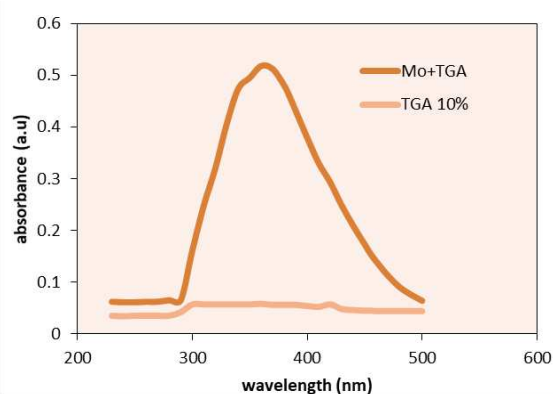
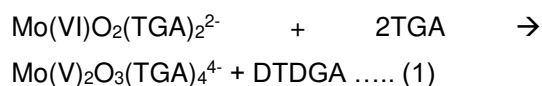


Figure 2. Absorption Curve for Molybdenum Thioglycolic Acid, Molybdenum 20 ppm and 200 μL TGA 10%

highly acid solution, Mo-TGA complexes has very low absorbance. The absorbance of complexes increased and became steady in the range pH 3 to 5 (11). Molybdenum was known could be reduced by TGA in two steps of reduction process from Mo(VI) to Mo(V) and from Mo(V) to Mo(IV) (10). Molybdenum, exists as stable Mo(VI), reacts with TGA to form $\text{Mo(VI)O}_2(\text{TGA})_2^{2-}$. Reduction process of Mo(VI) to Mo(V) occurred in pH range 4.5 to 6.0. Both of Mo(VI)-TGA and Mo(V)-TGA complexes has similar absorption curve at 370 nm. For each of Mo(VI) reduced, two TGA molecules will be oxidized to dithioglycolic acid (DTDGA).



Mo(V) as reduced product was identified by electrophoresis of reduced ^{99}Mo tracer. **Figure 3** shows electrophoregram of Mo(VI), Mo(V) and its complexes with TGA and KSCN. Mo(VI) in the solution with pH around 5 to 6 consist of three forms, there are $[\text{Mo}_7\text{O}_{24}]^{6-}$, $[\text{HMo}_7\text{O}_{24}]^{5-}$, $[\text{H}_2\text{Mo}_7\text{O}_{24}]^{4-}$ (12). Those peaks was identified in electrophoregram at 5 cm, 2 cm and 0 cm position respectively. When Mo(VI) was reduced to Mo(V) after TGA addition, those peaks became one peak as $\text{Mo(V)}_2\text{O}_3(\text{TGA})_4^{4-}$ species identified at 7 cm. This peak shifted to the positive direction of electrophoregam indicating $\text{Mo(V)}_2\text{O}_3(\text{TGA})_4^{4-}$ was formed.

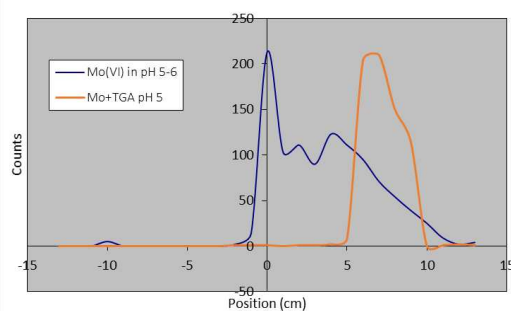


Figure 3. Electrophoregram of ^{99}Mo in pH 5-6 and ^{99}Mo reduced by TGA

After being reduced, Mo(V) theoretically reacts with SCN^- to form Mo-SCN complexes. According to **Figure 4**, no changes happened in Mo+TGA+KSCN absorption curve as evidence of those complexes has formed. This could be caused by stability of Mo(V)-TGA complexes in pH range 4.5-6.0. According to Hassanpour, Mo(VI) is able to form a complexes directly with thiocyanate (13), but in this study no absorption peak appeared in Mo(VI)+KSCN absorption curve. All blank of reagents were non absorbance species in UV-Vis region

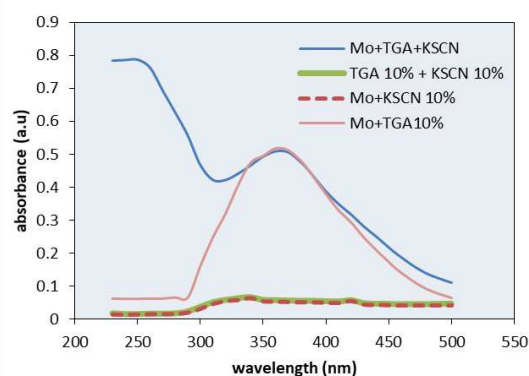


Figure 4. Absorption Curve for Mo+TGA, Mo+SCN, Mo+TGA+SCN and its blank at pH 6.0, 20 ppm of Mo

Effect of HCl Addition

When Mo-TGA-SCN mixture showed no evidence of Mo-SCN complexes formation in pH range 4.5-6.0, addition of 3 mL of 25% HCl instantly shifted peak of Mo-TGA from 370 nm to 460 nm indicating Mo-SCN complexes formation and solution color changed from yellow to orange (**Figure 5**). Higher absorbance (2 a.u) was reached for Mo(V)-SCN complexes at the same Mo concentration compared to Mo-TGA (0.5 a.u). Maximum absorbance of Mo-SCN is in the same wavelength with Fe-SCN (14), then the use of TGA could act as masking agent for Fe to prevent interference in molybdenum determination.

Addition of strong acid, for instance HCl, would suppress the equilibrium of thioglycolic acid ionization and weaken Mo-TGA complex (eq. 2 and 3), thus, SCN⁻ ligand could bind to Molybdenum as Mo-SCN complexes (eq. 4) (10).

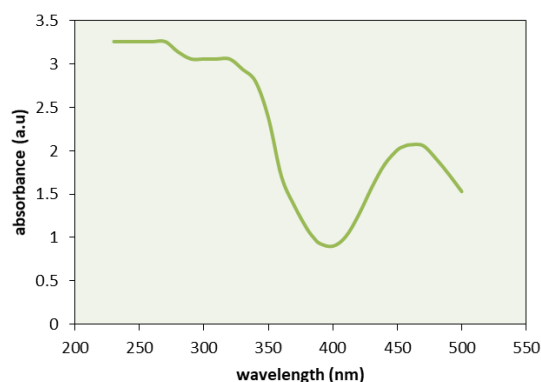
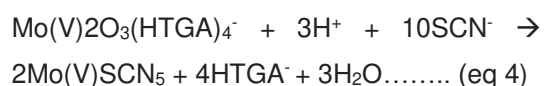
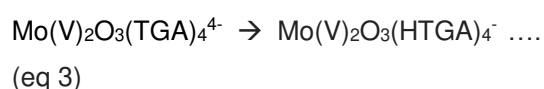


Figure 5. Absorption Curve of Mo-SCN with addition of 25% HCl

Formation of $\text{Mo(V)}_2\text{O}_3(\text{HTGA})_4^-$ complexes after addition of HCl was proven by electrophoregram. $\text{Mo(V)}_2\text{O}_3(\text{HTGA})_4^-$ peak shifted to 1 cm position of electrophoresis paper compared to $\text{Mo(V)}_2\text{O}_3(\text{TGA})_4^{4-}$ peak in 7 cm postion. $\text{Mo(V)}_2\text{O}_3(\text{HTGA})_4^-$ has less negative charge compared to $\text{Mo(V)}_2\text{O}_3(\text{TGA})_4^{4-}$. In other hand, Mo(V)SCN_5 is a neutral complexes with the peak in 0 cm postion in electrophoregram (**Figure 6**).

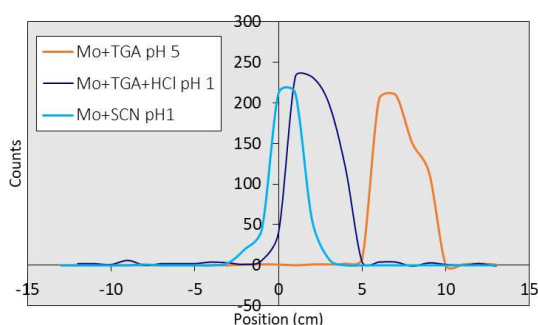


Figure 6. Electrophoregram of Mo+TGA in pH 5 and pH 1 after addition of HCl ; Mo+SCN complexes in pH 1

Amount of HCl added has the effect in the formation of Mo-SCN complexes. The optimum condition was the addition of 3 mL, 4 mL and 5 mL 25% HCl, 20 ppm Mo which gave the absorbance value 2.09 ± 0.032 , 2.08 ± 0.030 and 2.08 ± 0.025 respectively (**Figure 7**), but too much addition of HCl decreased the absorbance of Mo(V)SCN5 complex according to the Fig 7 with the addition of 6 mL HCl 25%. Thus, the formation of Mo(V)SCN complexes favors high acidity than mild-acidity. Like the oxidation effect in other metal (12), the addition of oxidating acid like HNO_3 and H_2SO_4 is not recommended because it would re-oxidize the Mo(V) to Mo(VI) and absorbance value would decreased as low as blank.

Optimization Study

There was a report about procedure in determination of molybdenum applying TGA as reductor, but it was a protocol without any study behind the steps in the protocol (5). This paper described the optimization study to acquire optimum condition of determination process.

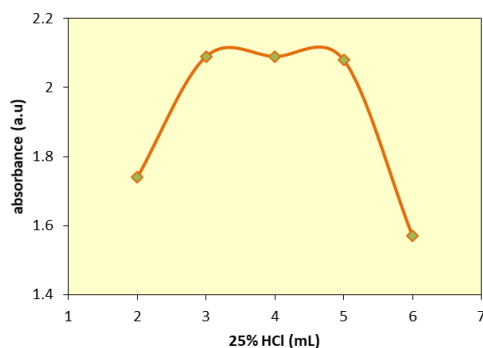


Figure 7. Effect of HCl addition in Mo-SCN absorbance (Mo 20 ppm, HCl 25%)

Addition of 0.2 mL to 0.3 mL of 10% thioglycolic acid into 20 ppm Mo solution provide stable absorbance for 20 ppm Mo solution as Mo-SCN complexes. Addition more TGA than optimum volume became less effective because no significant increase for the absorbance (**Figure 8**). In complexation with SCN^- , addition of 1 mL of 10% KSCN was sufficient enough initiate Mo-SCN complexes formation with more KSCN addition seems to be less effective (**Figure 9**). Thus, it can be concluded that addition of 0.2 mL 10% TGA and 1 mL 10% KSCN was selected in determination of Mo via Mo-SCN complexes

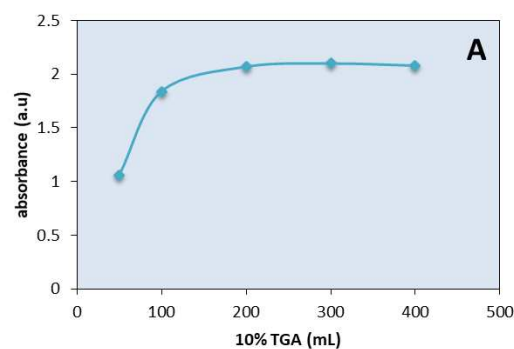


Figure 8. TGA optimization with 20 ppm Mo, 1 mL KSCN 10%, 4 mL 25% HCl

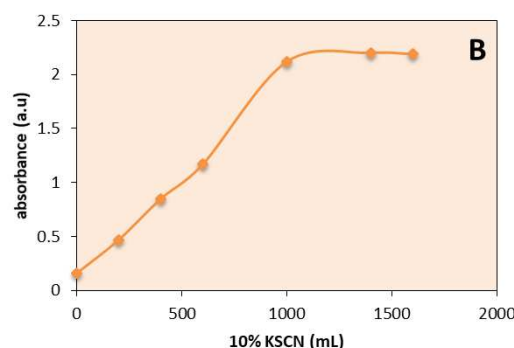


Figure 9. KSCN optimization with 20 ppm Mo, 300 μL TGA 10%, 4 mL 25% HCl

In order to determine stability of measurements in the range of time, stability test of Mo-SCN complexes was carried out. Mo-SCN complex was stable in room temperature for 2 hour based on the result in **table 1**. Further study must be carried out to find maximum duration of Mo-SCN stability. In 5 minutes of reaction, absorbance of Mo-SCN complexes was not at its maximum. From 10 minutes to 120 minutes, absorbance of Mo-SCN complex has been stable. This effect is relevant with the kinetic of complexes formation (14).

Determination of Molybdenum in ^{99m}Tc Solution Sample

Calibration curve in **Figure 9** was generated by absorbance measurement of molybdenum standard series using optimized condition.

Several measurements were carried out to obtain repeatability of molybdenum determination via TGA-SCN complexes. Result in table 2 shows that the method is linear for 2 to 30 ppm of Mo with linear regression 0.9988 ± 0.0007 from six repetition. Limit detection (LoD) for 7 repeated measurements of blank was 0.212 ppm.

Table 1. Stability of Mo-SCN Absorbance at Room Temperature and Ambient Atmosphere

Time (min)	Absorbance	
	Mo 5 ppm	Mo 10 ppm
5	0.65 ± 0.03	2.02 ± 0.02
10	0.71 ± 0.01	1.98 ± 0.03
30	0.73 ± 0.01	2.03 ± 0.01
60	0.71 ± 0.02	2.03 ± 0.02
120	0.72 ± 0.01	2.02 ± 0.01

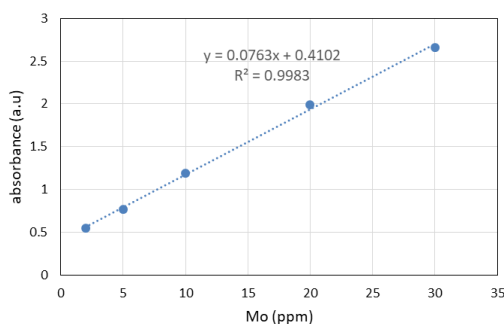


Figure 9. Calibration Curve for Mo 2 ppm to 30 ppm under optimized condition

From **Table 2** it can be concluded that Mo-TGA-SCN complexes is suitable for determination of molybdenum in ^{99m}Tc solution produced both from extraction method and electrodeposition method. Addition of oxalate and methyl ethyl ketone (MEK) as interfering factor did not alter measurement result.

The measurement of real sample was carried out and it was found that ^{99m}Tc solution from electrodeposition method has higher molybdenum content than ^{99m}Tc from extraction method (**Table 3**).

Table 2. Effect of Interfering Factor on Molybdenum Measurement

Interfering Factor	Absorbance	
	Mo 5 ppm	Deviation compared to no interference (%)
No interference	0.72 ± 0.01	0
MEK 1000 ppm	0.70 ± 0.02	0.027
Oxalic Acid 1000 ppm	0.72 ± 0.01	0
Fe 1000 ppm	0.73 ± 0.03	0.014

Table 3. Measurement of ^{99m}Tc Sample from Electrodeposition and Extraction Methods, (a) ⁹⁹Mo determined by Gamma Spectrometry (b) determined by UV-Vis Spectrophotometry

Sample	Impurities	
	⁹⁹ Mo ^a	Non radioactive Molybdenum ^b
Electrodeposition, ^{99m} Tc 5 mCi	0.51±0.11 µCi	10.52±1.34 ng
Electrodeposition, ^{99m} Tc 10 mCi	0.61±0.28 µCi	11.71±1.44 ng
Extraction, ^{99m} Tc 5 mCi	0.17±0.03 µCi	1.37±0.07 ng
Extraction ^{99m} Tc 10 mCi	0.21±0.05 µCi	2.24±0.15 ng

4. CONCLUSION

Spectrophotometric determination of molybdenum could be carried out via Mo-TGA-SCN complexes formation. In optimum condition, linearity of determination method was good with $r = 0.9988 \pm 0.0007$ from 2 ppm Mo to 30 ppm Mo. Limit detection of the method was 0.212 ppm. Interference did not distort the measurement when MEK, oxalic acid and technetium-99 were added as interfering factors. Validation process of measurement result must be carried out in the future to confirm the traceability of the molybdenum measurement using this method.

Summary of Procedure for Molybdenum Determination

1. Sample preparation : filtration and adjustment of pH into neutral condition should be carried out, strong oxidizing acid like sulfuric acid and nitric acid must be avoided or neutralized
2. Use 10 mL measurement flask as container for complexation

3. Up to 5 mL sample can be added into the flask

4. Reagent addition must be carried out in sequence : added 3 mL 25% HCl first followed by 200 µL of 10% TGA and 1 mL of 10% KSCN for the last

5. Wavelength calibration must be carried out before measurement, maximum absorbance of Mo-SCN complexes occurred near 460 nm wavelength

6. Standard calibration curve can be prepared with desired concentration of molybdenum, from 2 ppm to 20 ppm.

5. ACKNOWLEDGEMENT

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