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A Convenient Method on the Methyl-Ethyl-Ketone Extraction of $^{99m}TcO^-_4$

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=Abstract=

A convenient method of ^{99m}Tc-methyl-ethyl-ketone (MEK) extraction technique was developed and a mobile ^{99m}Tc-extraction generator was designed. The MEK extraction and the phase separation of $^{99m}TcO^-_4$ were carried out with a simple procedure in the same container.

The shielding of ^{99}Mo radioactivity was made with one lead container. The system was simplified by shielding $^{99m}TcO_4^-$(γ_e=0.14 MeV) separately. $^{99m}TcO^-_4$ in ^{99m}Tc-MEK extract was recovered by adsorption and elution only, and therefore, the possibility of volatilization was reduced. The volume of $^{99m}TcO^-_4$-saline product was reduced to 1 ml by using a small alumina column and the column operation time was shortened. The separation time of ^{99m}Tc was reduced to 30 minutes, and the operation was carried out at the outside of the shielding. The system was designed to operate under the condition of bacteria-free.

INTRODUCTION

Technetium-99 m, half-life of 6 hr, emits 0.14 MeV γ-ray only and is used mainly for medical diagnoses. ^{99m}Tc is produced as daughter of ^{99}Mo, long-lived parent nuclide, as follows:

$$^{99}\text{Mo} \xrightarrow[t_{\frac{1}{2}}=66.7\text{hr}]{\beta^-,\ \gamma} {}^{99m}\text{Tc} \xrightarrow[t_{\frac{1}{2}}=6.0\text{hr}]{\gamma=0.14\text{MeV}}$$

^{99}Mo is obtained from the separation of the fission products of uranium-235 and from the nuclear reaction of ^{98}Mo(n,γ) ^{99}Mo. ^{99}Mo, obtained by the fission of uranium-235, is carrier-free and is suitable for the production of a chromatographic ^{99m}Tc-generator. However, it has disadvantages that a large amount of radioactive wastes are produced: a considerable shielding and operating facilities are required: and the cost of production is high. If the neutron flux is not high enough, ^{99}Mo produced by (n,γ) reaction gives low specific activity, and therefore, it is not suitable for the production of a chromatographic generator. ^{99m}Tc is separated by the method of a complicated MEK extraction generator. The production of ^{99m}Tc by the fission of uranium-235 should be reviewed owing to the radioactive contamination of environment, and the imporovement of the extraction method in the reaction of

$$^{98}\text{Mo}(n,\gamma)\ {}^{99}\text{Mo} \xrightarrow{\beta^-} {}^{99m}\text{Tc},$$

which has less contamination problem, is prospective. The emphasis should be laid upon the worker's radiation protection. The method should be convenient and economical. Therefore, the extraction method should be simplified: a suitable chemical process should be developed: and the system should be shielded.

The MEK extraction method has been studied by several workers[1~3], modified

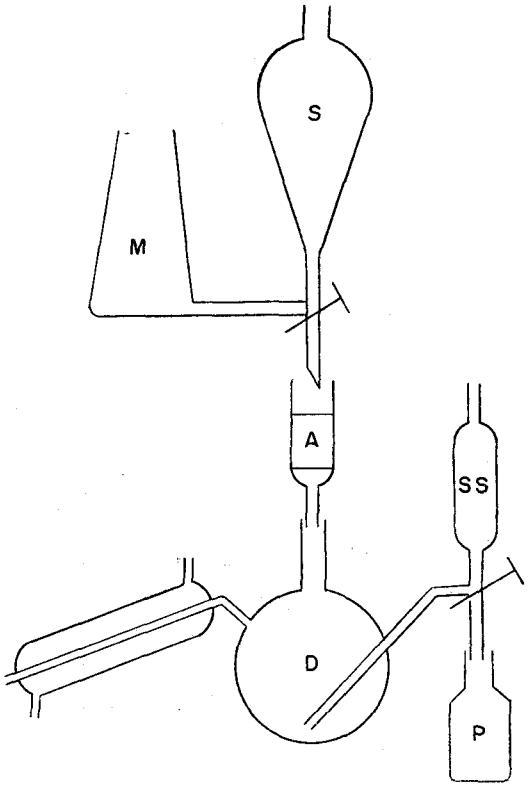

Fig. 1. ^{99m}Tc extraction by MEK.

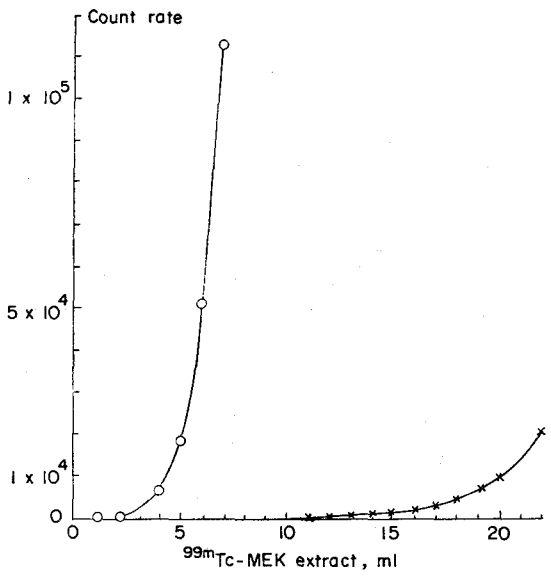

Fig. 2. Elution of ^{99m}Tc-MEK extract (None absorption of Na^+).
Alumina column: 1 cm×1 cm
o: Elution curve at pH 9.4
x: Eluation curve at pH 6.5

partly, and is in use at present. The procedure is as follows: $^{99}MoO_3$ is put into M container in Fig. 1, dissolved in alkali solution and mixed with MEK. After the mixture is transferred into separatory funnel S, ^{99m}Tc-MEK phase is separated from the aqueous phase, and passed through alumina A. From the effluent, MEK is evaporated at evaporator D and ^{99m}Tc is dissolved in a saline solution. Because MEK is combustible and the radioactive vapor is liable to leak, the procedure should be carried out at the chemical process unit in the hot cell. The evaporation of MEK is time-consuming and the residual ketone is likely to remain at the bottom. The facilities are needed a suitable space and great expenses, and the separation process is complicated. If the evaporation is eliminated, the separation time is shortened, and the facilities become simple and handling easier. As the gamma-ray energy of ^{99m}Tc is 0.14 MeV, the system is simplified by shielding ^{99}Mo (E_γ=0.74 MeV) separately.

In the MEK extraction method, the ^{99m}Tc-MEK separate solution is considered to contain small amounts of water, alkali and Mo. The small amounts of alkali are passed through the acidic alumina and remained into the product. If the alkali is relatively strong, ^{99m}Tc-MEK is passed through the alumina easily. But, in neutral, a portion of ^{99m}Tc is adsorbed on alumina (Fig. 2). If the alkali and the salt are eliminated from ^{99m}Tc-MEK, the alamina colum operation makes clear and the MEK evaporation can be omitted. If the extraction and the separation are carried out with one container, the shielding facilities are cut down. However, in the method of Tachimori et al.[4], the extraction and the separation are carried out with different

container, and therefore, the apparatus and the shielding can not be simplified, and the system should be designed to handle small volume for an injection. On the other hand, in the method of Baker et al.[3,5], the extraction and the separation are carried out with one container simultaneously. But the extraction efficiency is not good enough, and the MEK evaporation is not eliminated.

The time required for the sterilization and the bacteria-filtering is shortened by performing all the procedures under the condition of bacteria-free.

EXPERIMENTAL

In order to determine a condition of ^{99m}Tc-MEK extraction, the following experiments were carried out:

All the reagents are G.R. grade, and Dowex-50 cation exchange resin(200~400 mesh) and Brockman activity I alumina (acidic 80~200 mesh) Fisher Co. are used.

^{99m}Tc-MEK extract: $^{99m}MoO_3$ was neutron-irradiated at a D-ring, TRIGA mark III reactor, neutron flux 10^{13}n/cm^2·sec., for one week and dissolved in 500 ml of 6 N-NaOH, and then ^{99m}Tc was extracted with MEK.

1. pH

To estimate the alkaline strength of ^{99m}Tc-MEK extract, pH paper was immersed and the solution has shown pH between 6 and 10. In case of low pH, the extractant is clear and in high pH, the extractant is turbid.

2. Mo content

After ^{99m}Tc decayed, ^{99}Mo was measured by comparison of the activity of ^{99}Mo original solution and the Mo content in the ^{99m}Tc-MEK extract was 70 μg/ml and 12 μg/ml, respectively.

3. Alumina elution of ^{99m}Tc-MEK extract

Adsorption rates of $^{99m}TcO^-_4$ in MEK on alumina are affected by pH, salt concentration and water content, and the ^{99m}Tc-MEK extract contains a little amount of these materials irregularly, and compositely, and therefore, a column experiment was carried out. The ^{99m}Tc-MEK extract was passed through 1-cmϕ ×1-cm alumina column in Fig. 2. The column, 1-cmϕ×1-cm, was prepared to make a short elution time and a little elution volume. When the pH of ^{99m}Tc-MEK is high, ^{99m}Tc is eluted at the initial stage, and when the pH is relatively low, ^{99m}Tc is eluted at the latter stage, and therefore, it is difficult to adjust the elution condition.

4. Alumina column elution of $^{99m}TcO^-_4$

In order to wash MEK, that is, bed volume, during the operation of alumina column, the following experiment was carried out: After spotting $^{99m}TcO^-_4$ on alumina colum, water and MEK were passed through the column

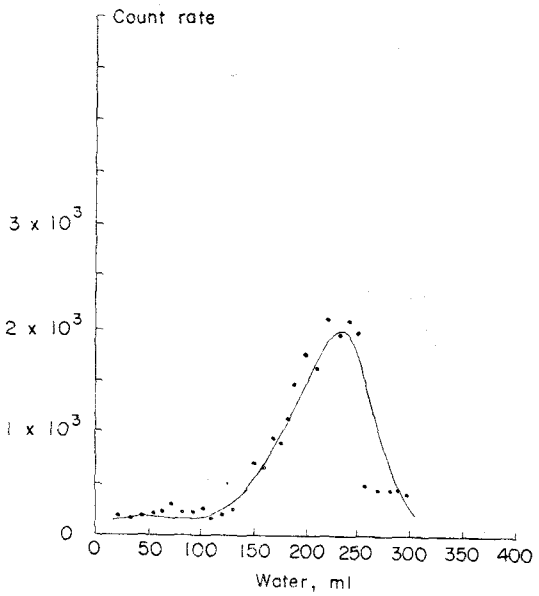

Fig. 3. Elution curve of $^{99m}TcO^-_4$ Eluent: H_2O Alumina column: 0.4-cmϕ×2-cm.

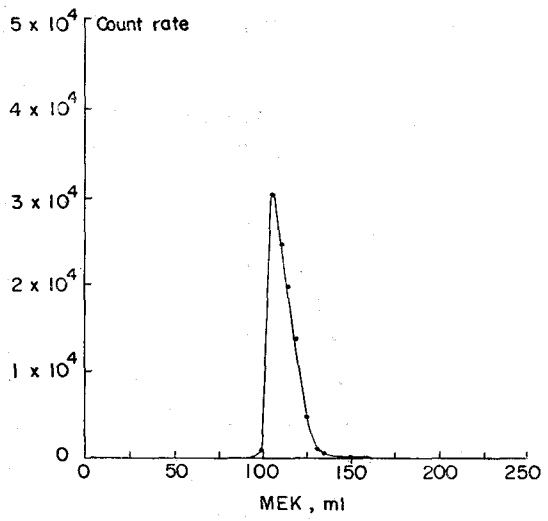

Fig. 4. Separation of ^{99m}Tc. Eluent: MEK Alumina column: 0.4-cmϕ×2-cm.

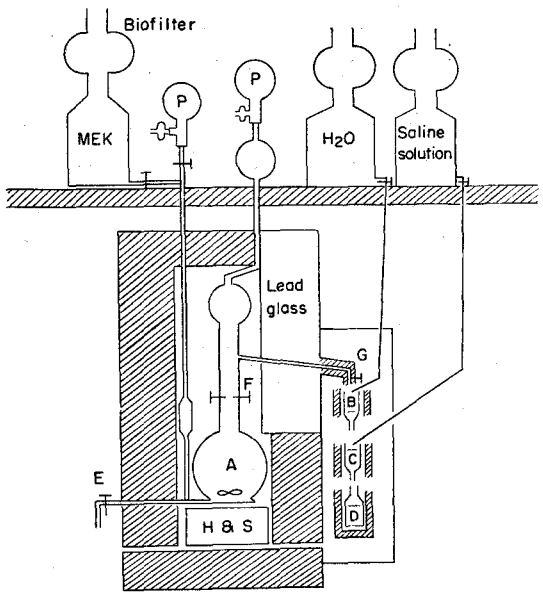

Fig. 5. ^{99m}Tc extraction apparatus
A: $^{99}MoO^-_4$ solution
B: Cation exchange column
C: Alumina colum
D: Penicillin bottle
E,G: Toflon cock
F: Electrode
P: ProPipet

and the elution was carried out as shown in Figs. 3 and 4.

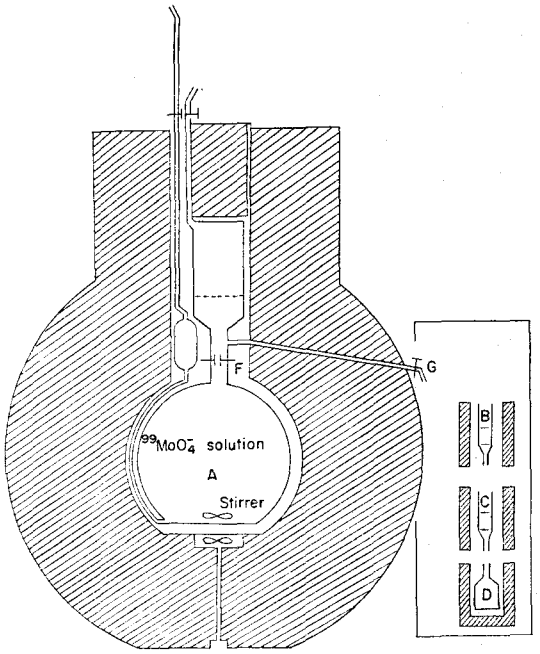

Fig. 5-1. ^{99m}Mo mobile ^{99m}Tc extractor.

5. Cation exchange column experiment of ^{99m}Tc-MEK extract

According to the relation of pH and turbidity on the pH experiment and the impurities on the elution experiments, 3 and 4, the removal of cation in the ^{99m}Tc-MEK extract and water, in which the impurity contains, is required. When ^{99m}Tc-MEK extract is passed through 1-cmϕ×1-cm cation exchange resin column, the measured pH of the ^{99m}Tc-MEK effluent is indicated is about 5.6.

6. Column elution of ^{99m}Tc-MEK extract by using cation exchange resin and alumina

Although metal ions were removed from the ^{99m}Tc-MEK extract, which was passed through the cation exchange resin column, the extract still contains a trace amount of anions and therefore, the elution was carried out with alumina column. The results on column elutions are shown in Figs. 6-1, 6-2 and 6-3. They are different from those results

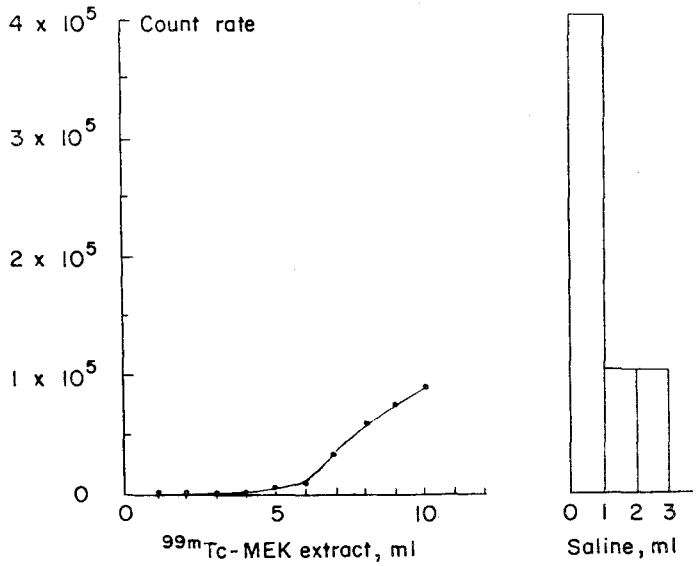

Fig. 6-1. Elution curve of ^{99m}Tc-MEK extract after absorption of Na^+ by cation exchange column. Alumina column: 0.4-cmϕ×2-cm.

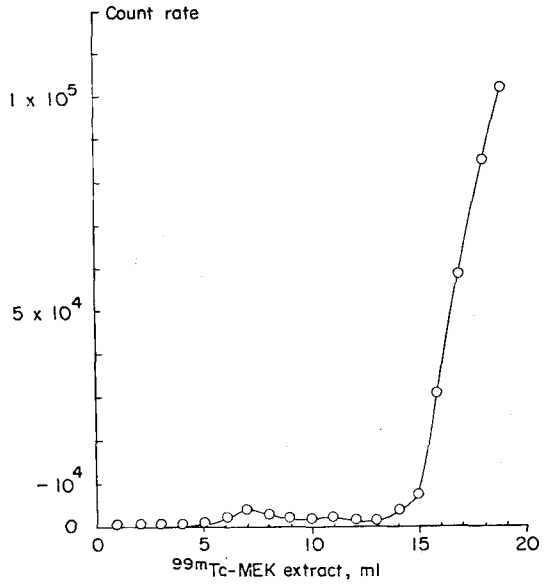

Fig. 6-2. Elution of ^{99m}Tc-MEK extract after absorption of Na^+ cation exchange colum. Alumina column: 1-cmϕ×1-cm.

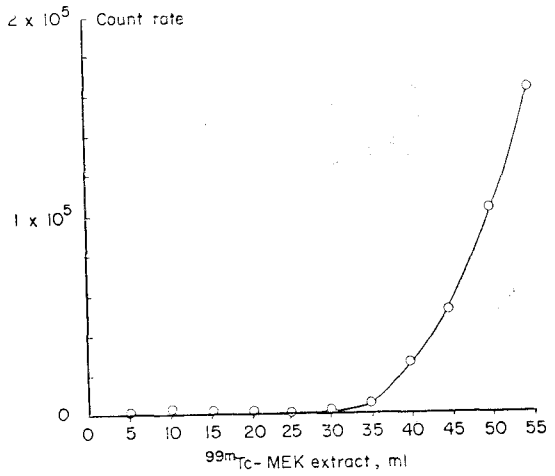

Fig. 6-3. Elution curve of ^{99m}Tc-MEK extract after absorption of Na^+ by cation exchange colum. Alumina colum: 1-cmϕ×4-cm. Flow rate: 1ml/min.

of $^{99m}TcO^-_4$ elution, experiment 4.

RESUTS

According to the results of the experiments, MEK extraction method was developed and the apparatus shown in Fig. 5 was designed, and then the experiments on the operation and the separation were carried out.

1. Apparatus

^{99}Mo original solution was put into a lead container for the radiation shielding, and the

apparatus was desinged to operate from the outside. The extraction and the separation from ^{99}Mo-alkali solution are carried out in one container, and low γ-ray energy ^{99m}Tc is handled with simple shield from the outside. In order to reduce the operation time and the volume of $^{99m}TcO^-_4$ solution, the size of ion exchange resin column and alumina colum was made 1-cmϕ×1-cm. The apparatus was set up into a bacteria-free container and the sterillization time was cut down through the bacteria-free operation with bacteria-free reagents.

Fig. 11 shows a supply tank for ^{99}Mo alkali solution, and Fig. 12 shows a bacteria-free container for cation exchange resin column and alumina column.

2. Procedure

After feeding a certain amount of ^{99}Mo-alkali solution into container (A) through cock (E), the following procedure is carried out:

(1) Add MEK into (A), and stir the mixture.

(2) After standing for a short time and separating phases, open cock (G) and pass the solution through a cation exchange column (B) and an alumina column (C).

(3) Wash the columns (B) and (C) with water to remove MEK residues.

(4) Add 1 ml of saline solution to the column (C) and pass 1 ml of the solution again through (C), and then receive it into a

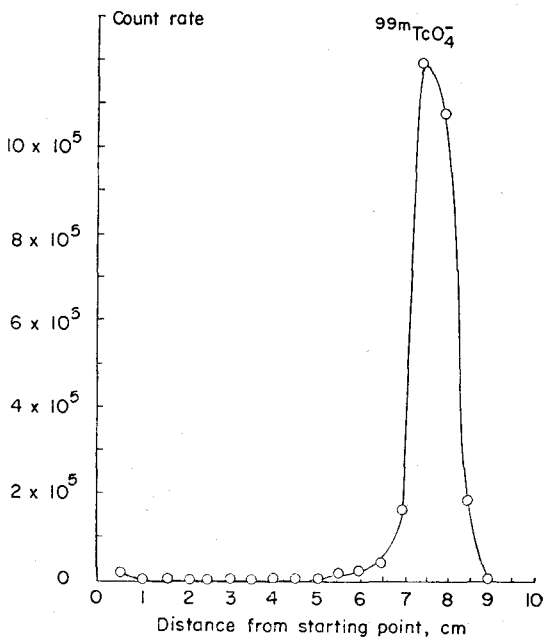

Fig. 7. Paper-chromatography of $^{99m}TcO_4^-$.

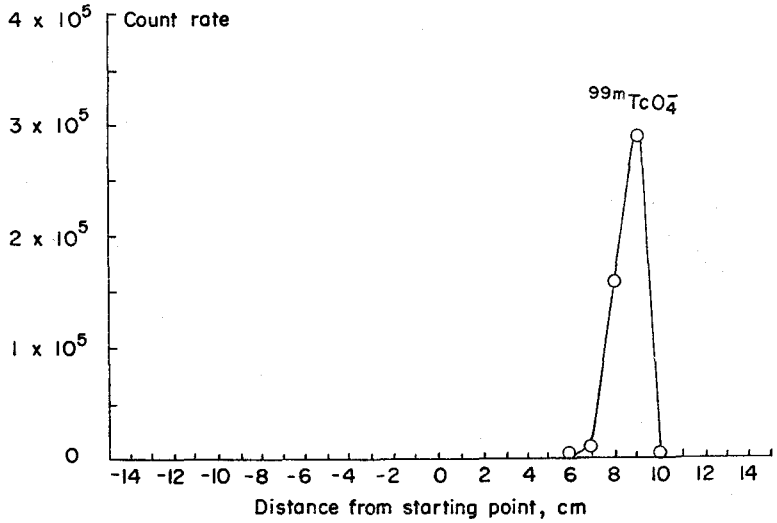

Fig. 8. Paper-electrophoresis of $^{99m}TcO^-_4$.

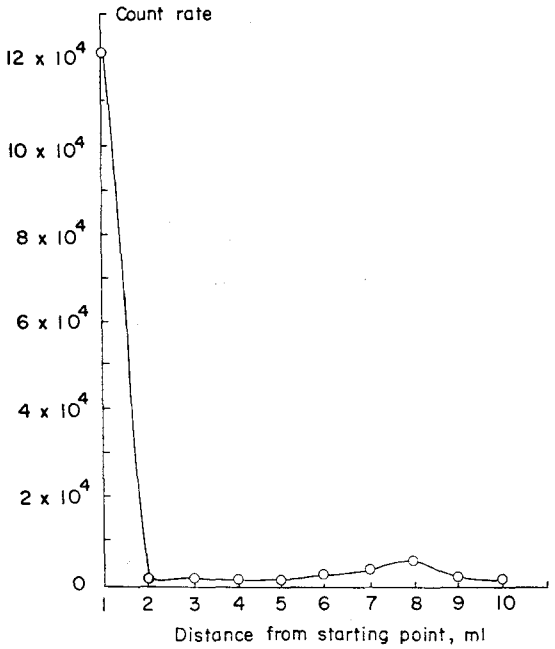

Fig. 9. Paper-chromatography of ^{99m}Tc-colloid.

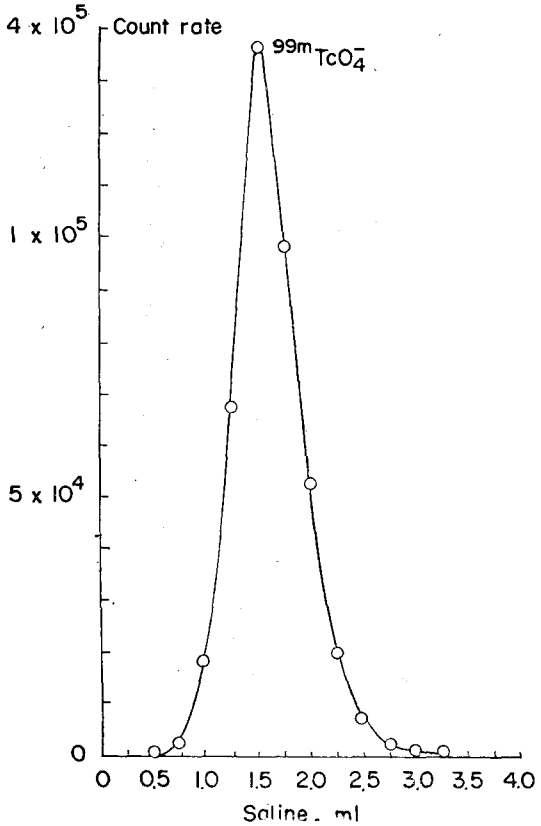

Fig. 10. $^{99m}TcO^{-}_{4}$ in saline effluent from alumina column. Column size: 1-cmϕ×1-cm.

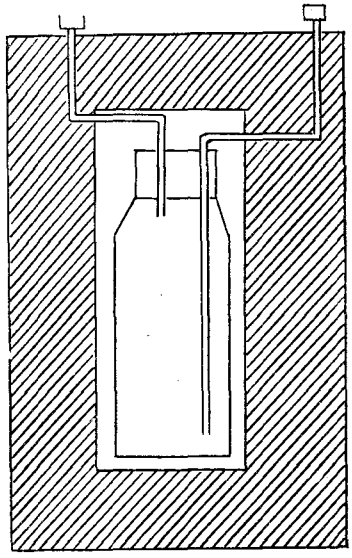

Fig. 11. ^{99}Mo supplier.

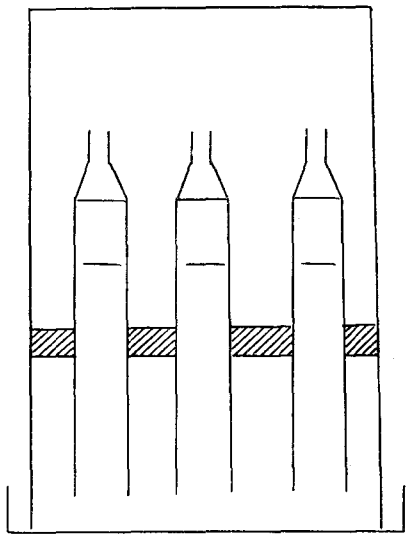

Fig. 12. Bacteria-free containers for cation cxchange resin column and alumina column.

penicillin bottle.

(5) The apparatus and the procedure are used over again, and the procedure is carried out in 30 minutes.

Loss of ^{99m}Tc from ^{99m}Tc-MEK extract is negligible during the procedure.

3. Quality control

The radioactive purity was over 99.999%,

and the molybdenum content was less than 10 μg/volume total. The radiochemical purity was determined by the paper-chromatography method and the paper-electrophoresis method, and the results are shown in Figs. 7 and 8. The result determined by the paper-chromatography method with a colloid solution, which was prepared, is shown in Fig. 9. The result separated as $^{99m}TcO^{-}_{4}$ in saline solution from the alumina column is shown in Fig. 10. The MEK content in the product was less than 0.1%.

CONCLUSION

(1) ^{99m}Tc-MEK extraction method has not been used extensively like chromatographic generator, because the method and the procedure are complicated, and therefore, the radiation shielding and the radioactive procedure have many disadvantages. This method and apparatus are a step advanced to 20 minutes by practice.

(3) Alumina, MEK and other impurities in the $^{99m}Tc^{-}_{4}$ product do not contain more than an adsoption capacity of alumina, because alumina column can wash sufficiently with water.

(4) The sterilization procedure and time are shortended by doing bacteria-free operation.

(5) As the radiation shielding is simplified, it is possible to prepare a mobile apparatus, which is used without hot-cell.

(6) Electronic automation of the apparatus is simplified as compared with ^{99m}Tc-chromatographic generator.

(7) The volume of $^{99m}TcO^{-}_{4}$ solution is reduced to about 1ml.

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$^{99m}TcO_4^-$의 메틸—에틸—케톤 간편 추출법

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요 약

간편형으로 ^{99m}Tc-메틸-에틸-케톤(MEK) 추출법을 개량하고 이동 가능형으로 ^{99m}Tc 추출 장치를 설계하였다. $^{99m}TcO^-_4$의 MEK추출 및 상 분리를 한 용기에서 하도록 하여 조작을 간편하게 하였으며 ^{99}Mo의 방사능 차폐를 한개의 납용기로 할 수 있도록 하였다.

$^{99m}TcO^-_4$(γ_e=0.14MeV)를 분리차폐를 하여 장치를 간소화하였다.

^{99m}Tc-MEK추출액중의 $^{99m}TcO^-_4$를 흡착 및 용리만에 의하여 회수할 수 있도록 하여 방사능 휘발 가능성을 줄이었고 알루미나 칼람을 소형으로 하여 $^{99m}TcO^-_4$염 제품의 부피를 1 ml로 줄이고 칼람 조작시간을 단축하였다.

^{99m}Tc 분리시간을 30분대로 줄이고 조작을 차폐밖에서 할 수 있도록 하였다. 장치를 무균 조작할 수 있도록 설계하였다.