

Evaluation of TBP, TOA and MEK as extractants to obtain ^{99m}Tc radiotracers in organic phase from $^{99}\text{Mo} / ^{99m}\text{Tc}$ generator

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Abstract

An alternative for radiotracer technique in Cuba, is the use of sodium pertechnetate ($\text{Na}^{99m}\text{TcO}_4$) eluted from $^{99}\text{Mo} / ^{99m}\text{Tc}$ generator. This radioisotope generator is produced by the Cuban Center of Isotopes (CENTIS). Taking into account that solvent extraction is an usual procedure to separate $^{99}\text{TcO}_4^-$ from the fission products, this technique was used to get a radiotracer in organic phase from the eluted $^{99m}\text{TcO}_4^-$, using 30% TBP-16% TOA/ n-dodecane and 30% TBP-16% TOA/ ciclohexane as solvents. On the other hand, MEK is used as solvent in the so called $^{99}\text{Mo} / ^{99m}\text{Tc}$ extraction radioisotope generator. Consequently, it was also evaluated. In this paper, the influence on the extraction degree, of the volumetric ratio between organic and aqueous phases, the time of phase shaking and the time elapsed between shaking-end and phase separation were studied. Furthermore, in the case of MEK, the influence of NaOH concentration in the aqueous phase was considered. For the extraction using 30% TBP-16% TOA/ciclohexane and 30% TBP-16% TOA/n-dodecane, the influence of pH was also studied. The extraction degree of $^{99m}\text{TcO}_4^-$ eluted from generator using MEK, as well as 30% TBP-16% TOA in n-dodecane or ciclohexane, in adequate conditions, was higher than 99%, so, any of the tested solvents could be used to get a ^{99m}Tc radiotracer in organic phase.

Key words: extraction, trioctylamine, tracer techniques, ketones, TBP

Evaluación del TBF, la TOA y la MEC como extrayentes para obtener radiotrazadores de ^{99m}Tc en fase orgánica a partir del generador de $^{99}\text{Mo} / ^{99m}\text{Tc}$

Resumen

Una alternativa para el empleo de la técnica de radiotrazadores en Cuba ha sido el uso del pertechnetato de sodio ($\text{Na}^{99m}\text{TcO}_4$) eluido del generador de $^{99}\text{Mo} / ^{99m}\text{Tc}$ producido en el Centro de Isótopos. Teniendo en cuenta que la extracción se utiliza regularmente para separar al $^{99}\text{TcO}_4^-$ de los productos de fisión, se evaluó este método para obtener un radiotrazador en fase orgánica a partir del $^{99m}\text{TcO}_4^-$, empleando como solventes la mezcla 30% TBF-16% TOA en n-dodecano y en ciclohexano. Por otro lado, la metiletilcetona se utiliza como solvente en el generador radisotópico de extracción de $^{99}\text{Mo} / ^{99m}\text{Tc}$, por lo que también se evaluó para estos fines. En el trabajo se estudió la influencia de la relación volumétrica de la fase acuosa y la orgánica, del tiempo de contacto en agitación y del tiempo de reposo antes de la separación de las fases, en el grado de extracción del ^{99m}Tc . En el caso de la metiletilcetona se evaluó además, la influencia de la concentración de NaOH en la fase acuosa y para la extracción, con 30% TBF-16% TOA en ciclohexano y en n-dodecano, la del pH. El grado de extracción del $^{99m}\text{TcO}_4^-$ eluido del generador empleando, ya sea la metiletilcetona o la mezcla 30% TBF-16% TOA en n-dodecano o ciclohexano, en condiciones adecuadas, fue superior al 99%; por tanto, cualquiera de los solventes evaluados se puede utilizar para obtener radiotrazadores de ^{99m}Tc en fase orgánica.

Palabras clave: extracción, trioctilamina, técnicas de trazadores, cetonas, TBP

Introduction

Studies which expand the potentialities of the ^{99m}Tc eluted from $^{99}\text{Mo} / ^{99m}\text{Tc}$ to label silts [1], surface waters in non-reducing [2,3,4] or reducing [5] environment have been carried out in our country. However, alternatives that allow the use of this isotope for labeling organic fluids have so far not been explored yet. Therefore, applications related with organic phase tracing have so far not been done in Cuba.

The application and development of nuclear energy goes by the treatment and confinement of its residuals, especially those with high activity which result from the re-processing of nuclear fuel. ^{99}Tc and ^{129}I radionuclides represent the dominant portion of the nuclear wastes with radiological risk [6].

Selective extraction with organic solvents is a commonly used procedure to separate $^{99}\text{TcO}_4^-$ from the rest of the fission products, with the objective of concentrating it before its final disposition. Tri-n-butylphosphate (TBP) and tri-n-octylamine (TOA) are two of the most used, either in self-sufficient form, in a mixture with diluters or in their one mixture. In all of these studies, the shaking times are between 10 and 15 min. Different diluents are use, among them: ciclohexane and n-dodecane [7-11].

On the other hand, it is also known that methylketone (MEK) is used as solvent in the so called $^{99}\text{Mo} / ^{99m}\text{Tc}$ radioisotope generator, which is produced nowadays by the Indian Radiation and Isotopic Technology Association [12].

The aim of the present work was to evaluate the extraction conditions of $\text{Na}^{99m}\text{TcO}_4$, eluted from $^{99}\text{Mo} / ^{99m}\text{Tc}$ radioisotope generator, using TBP, TOA and MEK as extractants in order to get a ^{99m}Tc radiotracer for organic fluids.

Materials and methods

General procedure for the extraction experiments

The extraction behavior of $^{99m}\text{TcO}_4^-$, eluted from the $^{99}\text{Mo} / ^{99m}\text{Tc}$ generator, was studied using MEK, 30% TBP-16% TOA/ n-dodecane and 30% TBP-16% TOA/ ciclohexane. The parameters were modified according to the goal of each experiment.

The aqueous and organic phases were shaken inside the 20 mL plastic syringe used as separator device. A German shaker ILMENAU-MLW was use and the shaking speed was kept constant. The volume of the aqueous phase was fixed at 3 mL, while the organic phase volume was modified.

After shaking and some resting time, three samples of 0.5 mL each were taken from aqueous phase and measured 3 times with NaI (Ti) detector joint to the ratemeter.

To evaluate the extraction yield, the extraction de-

gree, R (%), was determined as:

$$R(\%) = \left[\frac{B - A}{B} \right] * 100, \quad (1)$$

Where A (cps/mL) and B (cps/mL) are the radioactive concentrations of aqueous phase after and before extraction, respectively.

Each experiment was replicated 3 times for error estimation. Some studies were carried out using experimental design; in these cases the first experiment of the plan was performed 3 times.

Extraction of $^{99m}\text{TcO}_4^-$ with MEK

To study the influence on the extraction degree of the volumetric ratio of phases (V_o/V_a), NaOH concentration in the aqueous phase and time elapsed between shaking-end and phase separation (resting time), an experimental plan 2^3 was designed. R (%) was determined as the dependent parameter. Levels and modules (h) used for each parameter are shown in table 1. The experimental conditions were chosen taking into account previous experience [13].

Table 1. Levels and modules of the parameters used in the experimental plan for MEK

Level	X_1 V_o/V_a	X_2 c(NaOH) (mol/L)	X_3 Resting time (min)
Min	1	0.5	5
Max	4	5	10
h	1.5	2.25	2.5

Influence of shaking time on the extraction degree using MEK as solvent

Due to the short half life of ^{99m}Tc (6.02 h), it is important to reduce as much as reasonable possible the time consumed in radiotracer preparation. So, the behavior of the extraction degree was studies at the following shaking times: 1, 2, 4, 6, 8 and 10 min. NaOH concentration in the aqueous phase was 5 M, the resting time was 10 min and $V_o/V_a = 1$.

Extraction of $^{99m}\text{TcO}_4^-$ using 30% TBP-16% TOA/ ciclohexane and 30% TBP-16% TOA/ n-dodecane as solvents

To study the influence on the extraction degree of the volumetric ratio of phases, pH in the aqueous phase and time elapsed between the end of shaking and phase separation, an experimental plan 2^3 was designed. R (%) was again determined as dependent parameter. The aqueous solution pH was modified varying the concentration of HNO_3 . Table 2 shows the levels and modules (h) used for each parameter.

Table 2. Levels and modules of the parameters used in the experimental plans 2^3 for 30%TBP-16%TOA/ciclohexane and 30% TBP-16% TOA/n-dodecane extraction systems

Level	X_1 V_o/V_a	X_2 pH	X_3 Resting time (min)
Min	1	1	10
Max	4	4	15
h	1.5	1.5	2.5

Influence of pH on the extraction of $^{99m}\text{TcO}_4^-$ using 30% TBP-16% TOA in ciclohexane and n-dodecane as solvents.

As the extraction mechanism of $^{99m}\text{TcO}_4^-$ by TBP and TOA involves protons [7, 8, 16], the pH study was extended outside the performed experimental plans, (pH= 0.5 and 5). On the other hand, some points of the experimental designs were reproduced (pH=1, 2, 3 and 4) in order to validate the obtained mathematical models through the Kolmogorov Smirnov test. The shaking and resting times were fixed at 6 min and 10 min, respectively, and the phase volumetric relation was 1.

Influence of shaking time on the extraction of $^{99m}\text{TcO}_4^-$ using 30% TBP-16% TOA in ciclohexane and n-dodecane as solvents.

In this case, the extraction degree was determined after shaking 3, 6, 9, 12 and 15 min. The last one was the longest time reported in the consulted literature [11]. The resting time was 10 min, pH was fixed to 1, and $V_o/V_a = 1$.

Results and Discussion

Extraction of $^{99m}\text{TcO}_4^-$ with MEK

Results from the experimental plan are shown in table 3. Coefficients B1 (V_o/V_a) and B2 (NaOH concentration) resulting from the analysis of experimental data are positive, quite similar and significantly higher than B3 (resting time before phases separation), which influence on the extraction degree is also positive.

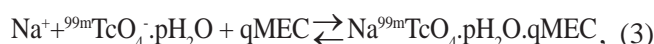
The best result (99.76 ± 0.04) % was obtained when all parameters had been fixed at maximum levels. If the resting time is reduced to 5 min, the extraction degree just decreases in 0.87%. This behavior agrees with the results obtained by Karpeles and Rivero [13] using MEK to separate ^{99m}Tc and ^{99}Mo from alkaline solutions. They found out the best extraction when NaOH concentration of aqueous solution was between 3 and 5 M. The design parameters were uncodified according to their modules and the model which describes its relationship with the extraction degree was established as (eq. 2):

$$R(\%) = 85.33 - 1.86 \left(\frac{V_o}{V_a} \right) + 0.38 * c(\text{NaOH}) + 0.46t - 0.09 \left(\frac{V_o}{V_a} \right) * t \quad (2)$$

Table 3. Results from the experimental plan 2^3 using MEK as solvent

Exp.	R(%)	Coefficients	
1	89.8 ± 0.1	B0 = 95.11	Variance: $S^2 = 0.011$ Degrees of freedom: 2 Probability: 95% Significant coefficients: B0 B1 B2 B3 B13
2	94.73 ± 0.04	B1 = 2.048	
3	94.3 ± 0.1	B2 = 2.258	
4	98.89 ± 0.04	B3 = 0.685	
5	91.6 ± 0.4	B12 = -0.09	
6	95.2 ± 0.1	B13 = -0.338	
7	96.5 ± 0.1	B23 = 0.088	
8	99.76 ± 0.04	B123 = 0	

MEK is a neutral extractant [14]. So, it is quite probably that extraction mechanism of $^{99m}\text{TcO}_4^-$ will be the hidration solvation (eq.3), through the coordination water [15].



Extraction of $^{99m}\text{TcO}_4^-$ using 30% TBP-16% TOA/ ciclohexane and 30% TBP-16% TOA/ n-dodecane as solvents

Table 4 shows results from the experimental design. All of the coefficients are statistically significant for a significance level of 0.05. The most important parameter is pH, which has a great negative influence in R (%). The lowest extraction degrees were obtained when pH was equal to 4 (experiments 3, 4, 7 and 8 from table 4). This perfectly matches with the roll of protons in the extraction mechanism for both extractants. Pruet et al. [7], El-Kot [16] and Kwan-Wook [8] stated that proton transferred by HNO_3 bonds to the phosphoric oxygen in TBP and $^{99m}\text{TcO}_4^-$ joins to the proton as a counter ion.

On the other hand, TOA is a tertiary amine with a pair of non-shearing electrons at nitrogen atom, which participate in the extraction mechanism. In this case, besides the protonation mechanism, extraction goes by ionic exchange [8].

For both extractant systems, the phase volumetric relationship influences in a positive way but, its effect on the extraction degree is only important only for pH = 4. Even using the higher phase volumetric relationship ($V_o/V_a = 4$) in experiments 2, 4, 6, and 6 from table 4, R(%) does not reach the values obtained when pH = 1 (exp. 1, 2, 5 and 6), no matter the phase of volumetric relationship used. It seems that as the total amount of active protons available for the extraction is smaller at pH = 4, the total amount of extractant molecules becomes a limiting factor.

Table 4. Results from the experimental plan 2³ using 30%TBP-16%TOA in ciclohexane or n-dodecane as solvents

Exp.	30%TBP-16%TOA/ciclohexane		30% TBP-16% TOA/n-dodecane	
	R(%)	Coefficients	R(%)	Coefficients
1	99.91 ± 0.01	B0 = 97.45	99.86 ± 0.01	B0 = 98.73
2	99.30 ± 0.02	B1 = 1.158	99.81 ± 0.04	B1 = 0.654
3	91.4 ± 0.2	B2 = -2.219	95.93 ± 0.02	B2 = -1.111
4	97.70 ± 0.02	B3 = 0.383	98.92 ± 0.04	B3 = 0.109
5	99.92 ± 0.01	B12 = 1.387	99.87 ± 0.02	B12 = 0.664
6	99.59 ± 0.01	B13 = -0.271	99.86 ± 0.01	B13 = -0.086
7	93.98 ± 0.04	B23 = 0.302	96.68 ± 0.06	B23 = 0.089
8	97.86 ± 0.02	B123 = -0.334	98.96 ± 0.01	B123 = -0.091
	Variance: S ² = 0.0005 Degrees of freedom: 2 Probability: 95% Significant coefficients: All		Variance: S ² = 0.0003 Degrees of freedom: 2 Probability: 95% Significant coefficients: All	

In fact, from all over the coefficients that represent interactions between parameters, B12 (phase volumetric relationship-pH) is the highest, even a little bigger than the influence of phase volumetric relationship itself. When $V_o/V_a = 1$ and pH = 4, the lowest extraction degree (91.4 ± 0.2) % was obtained.

As expected, the behavior of $^{99m}\text{TcO}_4^-$ extraction using n-dodecane as diluent instead of ciclohexane is similar. Nevertheless, the first one could be considered a little more efficient under the worst conditions (pH = 4 and $V_o/V_a = 1$), revealing a higher extraction degree (95.93 ± 0.02) %.

Finally, the extraction degree could reach (99.91 ± 0.01) % for ciclohexane and (99.86 ± 0.01) % for n-dodecane, if pH of aqueous solution is fixed to 1 with HNO₃, shaking time is 15 min and resting time is 10 min.

The parameters of the design were uncoded according to their modules and the model which describes its relationship with the extraction degree was established for 30% TBP-16% TOA/ciclohexane (eq. 4) and 30% TBP-16%TOA/n-dodecane (eq.5).

$$R(\%) = 106.1 - 1.74 \left(\frac{V_o}{V_a} \right) - 5.9 \text{pH} - 0.24t + 1.38 \left(\frac{V_o}{V_a} \right) * \text{pH} + 0.69 \left(\frac{V_o}{V_a} \right) * t + 0.23 \text{pH} * t - 0.06 \left(\frac{V_o}{V_a} \right) * \text{pH} * t \quad (4)$$

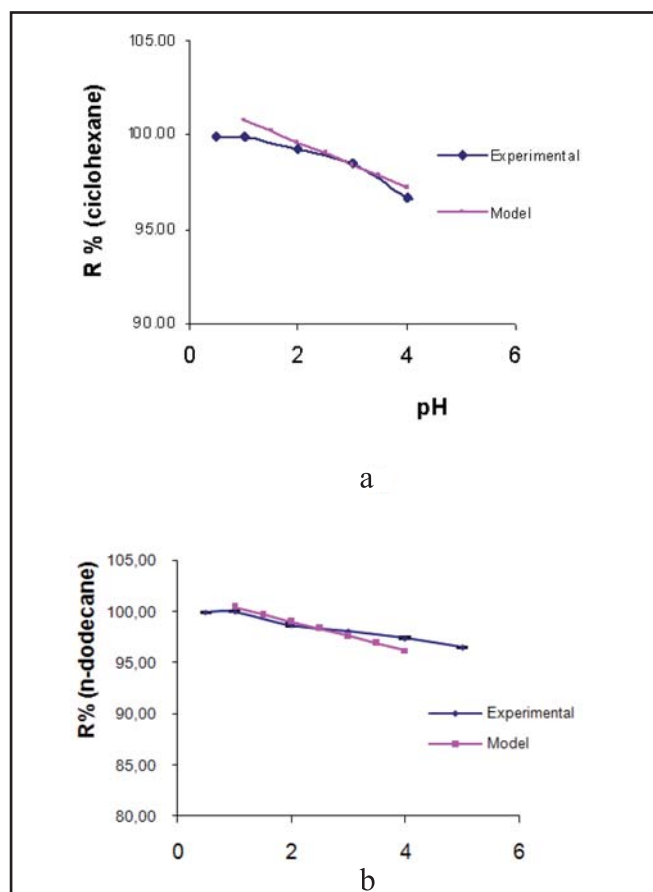
$$R(\%) = 102.1 - 0.52 \left(\frac{V_o}{V_a} \right) - 2.3 \text{pH} - 0.0007t + 0.5 \left(\frac{V_o}{V_a} \right) * \text{pH} + 0.02 \left(\frac{V_o}{V_a} \right) * t + 0.06 \text{pH} * t - 0.02 \left(\frac{V_o}{V_a} \right) * \text{pH} * t \quad (5)$$

Influence of pH on the extraction of $^{99m}\text{TcO}_4^-$ using 30% TBP-16% TOA in ciclohexane or n-dodecane as solvents

For 30% TBP-16% TOA/ciclohexane system (figure 1a), the experimental standard deviation varied bet-

ween 0.001 and 0.036. When n-dodecane was used as a diluent (figure 1b), values ranged between 0.02 and 0.12.

For both systems, the extraction degree decreases from pH = 1 to pH = 5 in approximately 4%. Nevertheless, R (%) is always higher than 95%, which could be enough for some radiotracing applications.


Figure 1. Behavior of R (%) versus pH using 30% TBP-16% TOA in ciclohexane (a) or n-dodecane (b) as solvents.

No significant differences were observed in the extraction degree at pH = 0.5 and 1. This increase on NO_3^- concentration does not induce yet, any significant negative effect on $^{99m}\text{TcO}_4^-$ extraction due to the competition of nitrates ions for TBP and TOA molecules [17, 18].

The Kolmogorov Smirnov test, for 95% of probability, demonstrated that there are not significant differences between experimental data and models.

Influence of shaking time on the extraction degree

Figure 2 shows the behavior of the extraction degree versus the increase on shaking time, when MEK was used as solvent. From 6 min on, no more significant increase in R (%) is observed and the value is about 96.5%. This matches with experiment 7 (table 3) where V_o/V_a was also 1. The standard deviations of the calculated extraction degrees oscillate between 0.05 and 0.20.

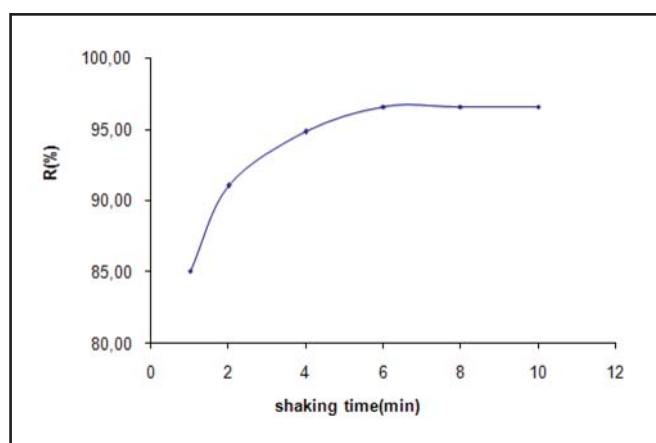


Figure 2. Behavior of R (%) versus shaking time, using MEK as solvent.

When using 30% TBP-16% TOA/ciclohexane, there are no significant changes on the extraction degree from 6 min on (figure 3a). The standard deviations ranged between 0.001 and 0.01. For 30% TBP-16% TOA/n-dodecane system (figure 3b), the standard deviations are in the same range, and the increase in the extraction degree from 6 to 15 min is just about 0.05%. So also in this case, 6 min of shaking time is enough for a successful extraction.

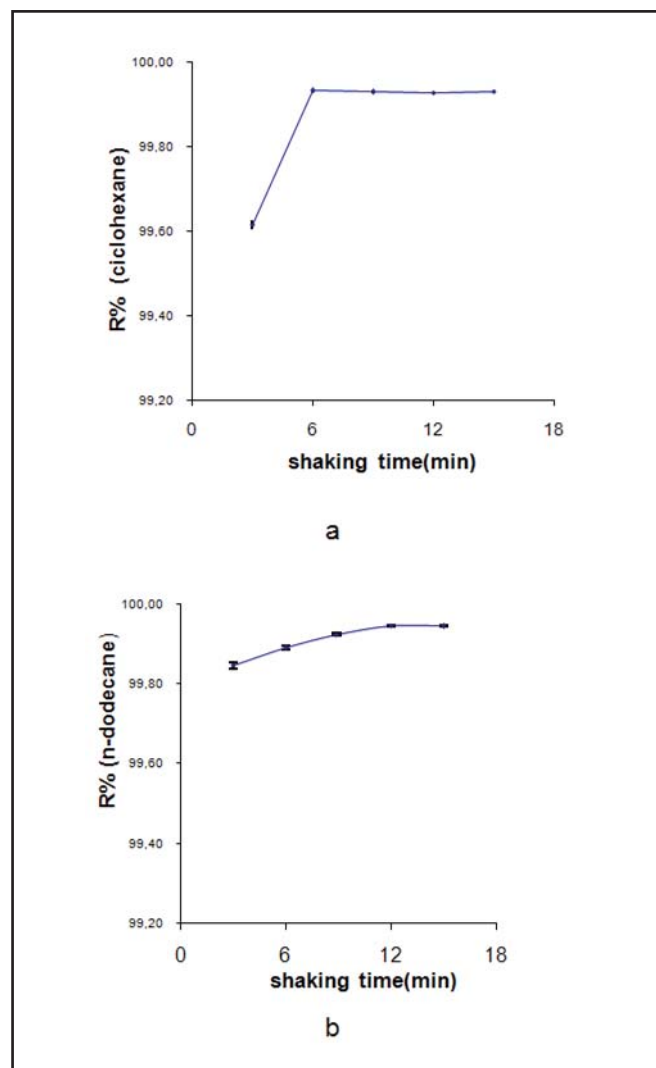


Figure 3. Behavior of R (%) versus shaking time, using 30% TBP-16% TOA in ciclohexane (a) or n-dodecane (b) as solvents.

Conclusions

When MEK was used as solvent, the best degree of extraction was obtained by fixing NaOH concentration in aqueous phase to 5 M, volumetric relationship (V_o/V_a) to 4, shaking time to 6 min and the resting time before phase separation to 10 min. The reduction of the resting time to 5 min provokes a diminishing of extraction degree just in a 0.87%. For 30% TBP-16% TOA/ ciclohexane and 30% TBP-16% TOA/ n-dodecane solvents, the best results were obtained by fitting the aqueous phase pH to 1 with nitric acid, shaking the phases during 6 min and separating them after 10 min of rest.

The solvent extraction of $^{99m}\text{TcO}_4^-$, eluted from $^{99}\text{Mo}/^{99m}\text{Tc}$ generator, using MEK and 30% TBP-16% TOA in n-dodecane or ciclohexane as solvents, could be used to get a radiotracer in organic phase for industrial applications. The selection of the solvent will depend on the nature of the system that will be traced and the cost-benefit analysis. Furthermore, it should be previously validated.

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