



Treatment and labeling of silica sand for obtaining a prospective solid ^{99m}Tc radiotracer

Luis Enrique Llanes Montesino¹ · Yuri Aguilera Corrales¹ · Ahmed Díaz Páez¹ · Yuniel Tejada Mazola¹ · Judith Domínguez Catasús¹ · Jorge Borroto Portela¹

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Abstract

Pretreated silica sand labeling using varying concentrations of tin(II) fluoride and chloride as reducing agents and different times labeling was performed in order to develop a methodology for labeling silica sand with ^{99m}Tc for using as solid radiotracer. Influence of different sand pretreatment parameters on the sorption yield ($R_{\text{ret}}\%$) was statistically evaluated. The effectiveness of the methods used to reduce pertechnetate ($^{99m}\text{TcO}_4^-$) by ascending paper chromatography was confirmed. Results show relatively high values of ^{99m}Tc sorption yields on silica sand. It was possible to establish a methodology for obtaining solid ^{99m}Tc labeled radiotracers in support of silica sand.

Keywords ^{99m}Tc solid radiotracer · Silica sand · Statistical experimental design.

Introduction

Radiotracers as a tool for various applications in the industry allow to carry out studies without stopping the technological flow of processes. However, this technique is still underutilized. The main cause is the lack of timely availability of required radiotracer [1]. Studies which expand the potentialities of ^{99m}Tc eluted from $^{99}\text{Mo}/^{99m}\text{Tc}$ generator to label silts [2], silica (FS) and zeolite (FZ) supported ferrogels, surface waters in non-reducing [3, 4], or reducing environment [5], and to trace the organic liquid phase [6], have been carried out in our country. Silica sand and others compounds with a high SiO_2 content are frequently used in industrial applications [7]. On the other hand, processes involving materials of similar density, granulometry and specific weight to the silica sand could also be studied with labeled silica sand [7]. The labeling of silica sand with ^{99m}Tc is shown as an attractive option to ensure the availability of radiotracers required in industrial applications.

Labeling of sands with radioisotopes has been approached previously [8, 9] using methods of activation of lanthanum oxides. Techniques of this type are not available in countries that don't have nuclear facilities for the activation of solid matrixes. The reduction method of $^{99m}\text{TcO}_4^-$ with tin(II) chloride (SnCl_2) for labeling of silica sand has been used by others authors [10]. These studies are still in a preliminary level. The labeling methodology is not very described in the literature neither sufficiently studied.

On the other hand, several authors in the Radiopharmacy field have used tin(II) fluoride (SnF_2) instead of the SnCl_2 to reduce the ^{99m}Tc , adding its smallest tendency to the hydrate and therefore its biggest storage stability [11–13].

In the present work, the pretreated silica sand was labeled by $^{99m}\text{TcO}_4^-$ reduction using different times labeling and varying concentrations of SnCl_2 and SnF_2 as reducing agents in order to get a solid ^{99m}Tc radiotracer for multi-phase flow studies. The purpose of this work is to evaluate the influence of different parameters on the pretreatment and labeling silica sand in order to obtain a prospective ^{99m}Tc solid radiotracer.

✉ Luis Enrique Llanes Montesino
Luis.LlanesMontesino@unige.ch

¹ Instituto Superior de Tecnologías y Ciencias Aplicadas de la Universidad de La Habana (InSTEC), Quinta de los Molinos, Ave. Salvador Allende y Luaces, Plaza de la Revolución, CP 10600 Havana, Cuba

Experimental

1 g of silica sand and 1 mL of $^{99m}\text{TcO}_4^-$ (ac) eluted from the $^{99}\text{Mo}/^{99m}\text{Tc}$ generator with 3 MBq of ^{99m}Tc activity were added in a tube for centrifuge. The mixture was stirred for a period of 15 min. Soon afterwards 2 mL of SnF_2 or SnCl_2 solution (pH=5) of varying concentration according to experiment, was added. The solution was stirred for a reaction time which varies in each experiment and it was centrifuged for 1 min. Three aqueous phase samples of 0.2 mL were taken and were measured three times with a radiometric system SRNIC-02, coupled to a NaI (TI) detector. To evaluate ^{99m}Tc retention in the silica sand, the retention degree ($R_{\text{ret}\%}$), was determined indirectly as:

$$R_{\text{ret}\%} = \left(\frac{A_b - A_l}{A_b} \right) \times 100, \quad (1)$$

where, A_l (cps mL $^{-1}$) and A_b (cps mL $^{-1}$) are the radioactive concentrations of ^{99m}Tc solutions, after and before the contact with the silica sand, respectively. Each experiment was repeated three times for error estimation. Some studies were carried out using experimental designs. In these cases, the error was calculated from three experiments in the center of the experimental plan. Cuban natural silica sand from Silica Sand Industrial Plant of Guane, Pinar del Río, was used.

Pretreatment of silica sand was conducted in two main stages. In the first, 15 g of silica sand was put in contact with 15 mL of concentrated nitric acid (HNO_3) and the mixture was stirred for 15 min ($t_{\text{HNO}_3\text{-sand}}$) in a magnetic stirrer. Vacuum filtration with 25 mL of distilled water was used to separate the silica sand from the liquid phase. After filtered sand spread in a peatry plate and allowed to dry with IR lamp for 30 min. For the second stage the solid was transferred to a beaker in which were added 15 mL of sodium hydroxide (NaOH) 2 mol L $^{-1}$ of concentration and kept in touch with constant stirring for 15 min ($t_{\text{NaOH-sand}}$), filtered under vacuum filtration and the solid was dried with IR lamp for 1 h.

Paper chromatography with acetone as mobile phase was employed to verify the percent of reduced $^{99m}\text{TcO}_4^-$ to ^{99m}Tc colloidal - hydrolyzated ($^{99m}\text{TcO}_2$, $^{99m}\text{TcO}(\text{OH})_2$ or $^{99m}\text{Tc}^{2+}$) with SnCl_2 or SnF_2 . Afterwards 2 mL of SnCl_2 or SnF_2 solution of varying concentration were added (according to experiment) to 1 mL of $^{99m}\text{TcO}_4^-$ (ac) and the solution was stirred for the proposed reaction time for each experiment. A drop is removed and placed at the origin of the paper strip, this was placed in the tank to chromatography (glass jars) containing acetone (2 mm deep) with the end of the origin downwards. When the front of the run was moved by the paper strip, this is removed and allowed to dry. The center strip was cut and measured in SRNIC-02 system, coupled

Table 1 Parameters levels used for 2⁴ experimental design

Level	c(NaOH) (mol L $^{-1}$)	V(HNO $_3$)/m(sand) (mL g $^{-1}$)	$t_{\text{HNO}_3\text{-sand}}$ (min)	$t_{\text{NaOH-sand}}$ (min)
Line + 1	3.0	1.5	20	20
Line - 2	1.0	0.5	10	10
Line 3 0	2.0	1.0	15	15

to a NaI (TI) detector [5, 6]. To evaluate the reduced ^{99m}Tc retention by chromatography, the reduction yield ($R^*\%$) was determined as:

$$R^*\% = \frac{A_a}{(A_a + A_f)} \times 100 \quad (2)$$

where A_a (cps mL $^{-1}$) is the radioactive concentration at the point of application and A_f (cps mL $^{-1}$) is the radioactive concentration in the solvent front. Yields are reported with standard deviations reflect three replicates, and three measurements per replicate for a total of 9 radiometric measurements for each value of $R^*\%$.

The type of reducing agent (SnCl_2 or SnF_2) influence on ^{99m}Tc retention in the silica sand ($R_{\text{ret}\%}$) was evaluated. Two experiments were carried out using 15 min of reaction time and 0.5 mmol L $^{-1}$ of concentration for each reducing agent. These conditions were chosen from previous studies results [10, 14].

A 2² factorial experimental plan was designed to study the influence of SnF_2 concentration and reaction time on ^{99m}Tc retention in the solid. The maximum and minimum values of the plan used were 30 min and 15 min of reaction times, and 2 mmol L $^{-1}$ and 0.5 mmol L $^{-1}$ of SnF_2 concentrations, respectively. Parameters values were selected taking into account the divergence from bibliographic reports and previous results [10, 15].

Some experiments to evaluate the influence on the ^{99m}Tc retention degree of the c(NaOH), relation V(HNO $_3$)/m(sand), reaction time between HNO $_3$ and sand ($t_{\text{HNO}_3\text{-sand}}$) and reaction time between NaOH and sand ($t_{\text{NaOH-sand}}$) used for the pretreatment of the silica sand, were executed. A 2⁴ factorial experimental plan was designed. Limits and the middle values of the plan used for each parameter are shown in Table 1. Parameters values were selected taking into account the divergence from bibliographic reports and previous results [10].

The data was processed with STATGRAPHICS Centurion XV software. P values for 5% degree of confidence were selected to determine statistical significance of the principal effects as well as the interactions. Three replicates were performed in the center of the plane to assess the pure error

Table 2 Reduction yields ($R^*_%$) and ^{99m}Tc retention degrees ($R_{\text{ret}\%}$) obtained using SnCl_2 and SnF_2 as reducing agents

	Reducing agent	Reaction time (min)	c(Reducing agent) (mmol L^{-1})	$R^*_% \pm \sigma$	$R_{\text{ret}\%} \pm \sigma$
Line 1	SnCl_2	15	0.5	89 ± 2	49 ± 1
Line 2	SnF_2	15	0.5	99.2 ± 0.4	69.1 ± 0.1

Table 3 Results from the 2^2 experimental design

	A	B	$R_{\text{ret}\%}$	Factor	P value
Line 1	2.0	15	68.1 ± 0.4	A: c(SnF_2) (mmol L^{-1})	0.7822
Line 2	2.0	30	30.9 ± 0.5	B: reaction time (min)	0.002
Line 3	0.5	15	68.4 ± 0.4	AB	0.6940
Line 4	0.5	30	29.5 ± 0.7	Lack of fitting	0.6503
Line 5	2.0	15	69.1 ± 0.5		
Line 6	2.0	30	31.4 ± 0.6		
Line 7	0.5	15	69.5 ± 0.3		
Line 8	0.5	30	30.5 ± 0.4		
Line 9	2.0	30	29.5 ± 0.7		

In order to meet the transformations in silica sand after treatment a study of X-ray spectroscopy coupled to the technique of scanning electron microscopy (SEM-EDS) to samples of silica sand was made before and after treatment. For treatment of it there were employed $c(\text{NaOH}) = 1 \text{ mol L}^{-1}$, $V(\text{HNO}_3)/m(\text{sand}) = 1.5$, $t_{\text{HNO}_3\text{-sand}} = 20 \text{ min}$ and $t_{\text{NaOH-sand}} = 20 \text{ min}$

Results and discussion

With the purpose of relating the quantity of reduced $^{99m}\text{TcO}_4^-$ ($R^*_%$) with the obtained retention degree ($R_{\text{ret}\%}$) the chromatographic study of the reduction of the $^{99m}\text{TcO}_4^-$ was carried out. The results show that the reduction yields

($R^*_%$), with both reducing agents, were much higher than retention degrees obtained (Table 2), therefore there is a greater amount of reduced ^{99m}Tc species adsorbed on the surface of silica sand [12, 16].

Table 2 shows that obtained values ($R_{\text{ret}\%}$) using SnF_2 are higher by approximately 20% than those obtained under the same conditions using SnCl_2 , probably due to the greater stability of SnF_2 reducing properties [17].

There are different approaches in the literature about the influence of SnF_2 concentration and reaction time on ^{99m}Tc retention in the silica sand [10]. The $R_{\text{ret}\%}$ obtained from the 2^2 executed experimental design and P values for the principal effects as well as for their interactions are shown in Table 3. From the P value analysis, it was clear that just the variation of reaction time (B) between SnF_2 and $^{99m}\text{TcO}_4^-$ is statistically significant ($P = 0.002$). There is only a 0.2% probability that variation observed in the $R_{\text{ret}\%}$ due to variation of parameter B could be by chance. The remaining factors (A and AB) are not statistically significant for a 95% confidence.

The highest ^{99m}Tc sorption yields were obtained for experiments where corresponding reaction times were employed at the minimum level (15 min), indicating that the increase of this factor has a negative effect on the degree of ^{99m}Tc retention.

Equation 3 describes the dependency between the $R_{\text{ret}\%}$ and the studied parameters. Lack of fitting P value (0.6503) greater than 0.05 indicates that the model properly represents the behavior of the $R_{\text{ret}\%}$ for a 95% of confidence in the studied interval.

$$R_{\text{ret}\%} = 112.462 + 1.213 \times c(\text{SnF}_2) - 2.894 \times t + 0.0657 \times c(\text{SnF}_2) \times t \quad (3)$$

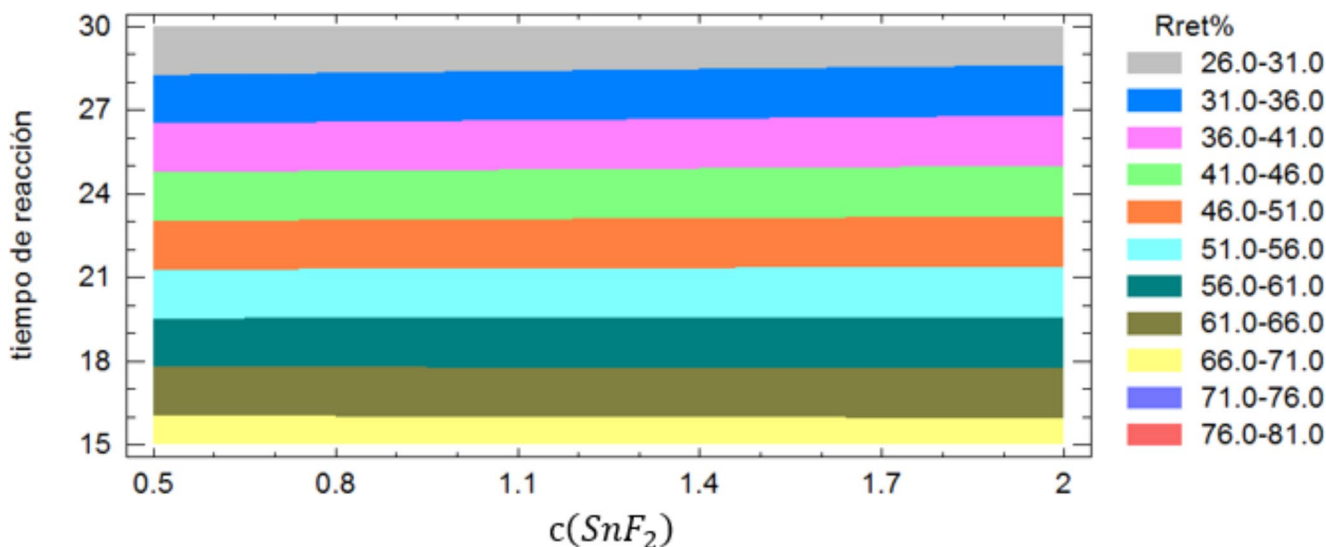


Fig. 1 Response surface of the $R_{\text{ret}\%}$ model calculated with the 2^2 experimental design

Table 4 Results of the chromatographic study of $^{99m}\text{TcO}_4^-$

	Reaction time (min)	c(SnF ₂) (mmol L ⁻¹)	R* % ± σ
Line 1	15	0.5	99.2 ± 0.4
Line 2	15	2	99.0 ± 0.2
Line 3	30	0.5	76 ± 1
Line 4	30	2	82 ± 2

It is possible that with increasing reaction time the reduced ^{99m}Tc is re-oxidized and become part of the solution, then the retention degree of ^{99m}Tc decrease. The labeling of the silica sand was performed after each stage of treatment in order to determine the influence of these stages on the ^{99m}Tc sorption yields. Withholding grades earned during each stage of treatment were $35 \pm 1\%$ for reaction with HNO_3 (conc), $37 \pm 2\%$ for the attack with NaOH (concentration of 2 mol L^{-1}) and $70 \pm 2\%$ for the full treatment, showing that the two stages of treatment have great significance sand, each being responsible for approximately 50% of the value of $R_{\text{ret}\%}$ obtained. Therefore, it is convenient to study the influence of several parameters related with both stages of the treatment of the sand silica in the degree of retention of the ^{99m}Tc

Response surface of the $R_{\text{ret}\%}$ model calculated is shown in Fig. 1. This allows to predict the $R_{\text{ret}\%}$ with the variation of the factors within limits established in the design.

The results of chromatographic study in order to explore the cause of the negative effect of reaction time on the degree of ^{99m}Tc retention (Table 4) show a decrease in the values of $R_{\text{ret}\%}$ with increasing reaction time for both concentrations

of reducing agent. This is probably the main cause of the decrease in the degree of retention of ^{99m}Tc in the treated silica sand with increasing to 30 min of reaction time.

Table 5 shows the results from 2⁴ experimental design. From the P value analysis, it was clear that only factors B ($V(\text{HNO}_3)/m(\text{sand})$) and C ($t_{\text{HNO}_3\text{-sand}}$), within established limits, had significant effects on the degree of ^{99m}Tc retention. So, the observed variations in the $R_{\text{ret}\%}$ are mainly provoked for the variation of the relation $V(\text{HNO}_3)/m(\text{sand})$ and the reaction time between HNO_3 and sand.

Indeed, higher $R_{\text{ret}\%}$ values were obtained in experiments 1, 10, 17 and 19, which matched the maximum of $V(\text{HNO}_3)/m(\text{sand})$ and $t_{\text{HNO}_3\text{-sand}}$, and the experiment 2, which corresponds to maximum value of $t_{\text{HNO}_3\text{-sand}}$, all obtained values are above 70%.

Figure 2 shows the semi-quantitative analysis of the composition of the silica sand sample before and after treatment, obtained by X-ray spectroscopy coupled to the technique Microscopy Scanning Electron Microscopy (SEM-EDS).

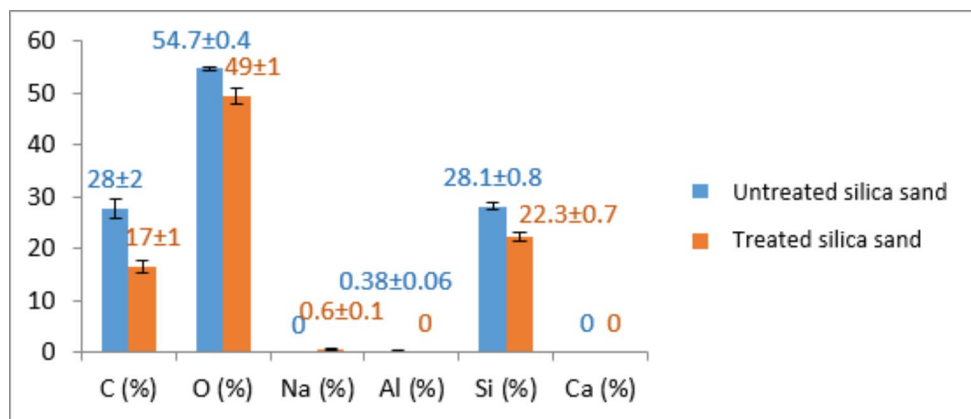
These results show the effect of each stage of the treatment, the first with HNO_3 to clean the sand of organic matter, which is reflected in the study with the variation of the contents of oxygen and carbon. With the removal of these impurities are released pores on the surface of the grains that were previously occupied by them. During the second stage (treatment with NaOH) can modify the crystalline structure

Table 5 Results from the 2⁴ experimental design

	A	B	C	D	$R_{\text{ret}\%} \pm \sigma$	Factor	P value
Line 1	3.0	1.5	20	10	72.4 ± 0.5	A: c(NaOH) (mol L ⁻¹)	0.7928
Line 2	1.0	0.5	20	20	71 ± 1	B: $V(\text{HNO}_3)/m(\text{sand})$ (mL g ⁻¹)	0.0243
Line 3	1.0	0.5	10	20	67 ± 1	C: $t_{\text{HNO}_3\text{-arena}}$ (min)	0.0009
Line 4	3.0	0.5	20	20	65.7 ± 0.8	D: $t_{\text{NaOH-arena}}$ (min)	0.2376
Line 5	1.0	1.5	10	10	67.3 ± 0.8	AB	0.4536
Line 6	2.0	1.0	15	15	69.0 ± 0.2	AC	0.6566
Line 7	1.0	1.5	10	20	67.3 ± 0.9	AD	0.6380
Line 8	3.0	1.5	10	20	68.2 ± 0.2	BC	0.3204
Line 9	3.0	0.5	10	10	64 ± 1	BD	0.6380
Line 10	1.0	1.5	20	10	71.2 ± 0.3	CD	0.2663
Line 11	2.0	1.0	15	15	69.0 ± 0.2		
Line 12	3.0	0.5	10	20	68.1 ± 0.7		
Line 13	2.0	1.0	15	15	69.5 ± 0.3		
Line 14	3.0	1.5	10	10	66.5 ± 0.2		
Line 15	1.0	0.5	20	10	70.2 ± 0.5		
Line 16	1.0	0.5	10	10	64.1 ± 0.4		
Line 17	3.0	1.5	20	20	74.5 ± 0.5		
Line 18	3.0	0.5	20	10	71.0 ± 0.4		
Line 19	1.0	1.5	20	20	73.9 ± 0.5		

The effect of $t_{\text{NaOH-sand}}$ parameter is not excluded from the analysis because their P-value shows that only 23% of the $R_{\text{ret}\%}$ variation due to the variation of this factor from the minimum level to the maximum is due to chance. It is recommended to keep at its highest level. With the increase over the initial methodology pretreatment sand of relation $V(\text{HNO}_3)/m(\text{sand})$ from 1 to 1.5 and $t_{\text{HNO}_3\text{-sand}}$ in 5 min (from 15 to 20 min) is achieved increase $R_{\text{ret}\%}$ to about 5% (from $69.2 \pm 0.2\%$ to $74.5 \pm 0.5\%$)

Fig. 2 Semi-quantitative analysis of the silica sand composition by SEM-EDS



of SiO_2 , thereby increasing the available sites for adsorption. This is reflected from the silicon content decreased as from forming a gel of soluble silicate, this contact is washed with water and no longer part of the crystal structure [18]. The results discussed above suggest that the $R_{\text{ret}\%}$ increased after treatment, are mainly due to the observed changes in silica sand chemical composition and structure.

Conclusions

The retention degree of $^{99\text{m}}\text{Tc}$ increase from $48.7 \pm 1.4\%$ when SnCl_2 is used as reducing agent to $69.1 \pm 0.1\%$ with SnF_2 . So, the obtained results indicate that SnF_2 is prospective for the labeling procedure. It can be stated with 95% confidence that in the range studied, the reaction time between SnF_2 and $^{99\text{m}}\text{TcO}_4^-$ influences negatively on the labeling of treated silica sand, while the concentration of SnF_2 does not influence. It is recommended to use 15 min as reaction time and $c(\text{SnF}_2) = 0.5 \text{ mmol L}^{-1}$ for labeling. The SEM-EDS analysis showed that the pretreatment of silica sand favors the $^{99\text{m}}\text{Tc}$ retention, probably due to the changes observed in its chemical composition and structure. Using 20 min for both reaction times ($t_{\text{HNO}_3\text{-sand}}$ and $t_{\text{NaOH-sand}}$), relation $V(\text{HNO}_3)/m(\text{sand}) = 1.5$ and $c(\text{NaOH}) = 1 \text{ mol L}^{-1}$ for silica sand treatment a $^{99\text{m}}\text{Tc}$ retention degree of $74.5 \pm 0.5\%$ could be obtained. From the obtained results for treatment and labeling of Cuban silica sand, it was possible to establish an optimum methodology to obtain a solid $^{99\text{m}}\text{Tc}$ radiotracer for industry purposes.

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