



Ultra-fast, selective and pseudo-quantitative analysis of ^{99}Tc in nuclear waste for screening purposes

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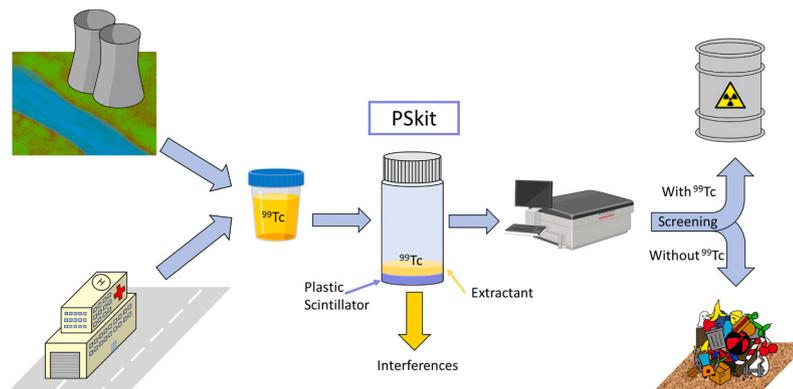
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HIGHLIGHTS

- A new detection method for ^{99}Tc selective screening analysis has been developed.
- PSkits can perform the ultrafast analysis of ^{99}Tc in liquid samples.
- PSkits have been validated by measuring ^{99}Tc in simulated nuclear reactor waste and spiked urine samples.
- ^{99}Tc analysis with PSkits can be performed in presence of radioactive interferences.
- Analysis with PSkits will simplify and facilitate characterization of nuclear waste leading to efficient classification and disposal.

GRAPHICAL ABSTRACT



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ABSTRACT

Controlling radioactivity is essential in various fields, such as the decommissioning of nuclear power plants and nuclear medicine. In some cases, a full characterization of samples is not required; instead, a screening analysis that provides an overall indication of the activity present can be sufficient to determine if a sample is radioactive. This article introduces a new system called PSkits designed specifically for ultra-fast and selective screening detection of ^{99}Tc . PSkits consist of a plastic scintillation layer attached to the bottom of a scintillation vial, coated with aliquat-336® as a selective extractant. In this study, the preparation of PSkits was optimized by adjusting the proportions of crosslinker, porogen, and the type of vial used. The analysis method was developed, and the selectivity against common interferences was tested by optimizing the rinsing media. Finally, PSkits were validated by analysing simulated nuclear waste samples and urine spiked samples, achieving satisfactory results with quantification errors below 50 %, demonstrating their effectiveness for the intended purpose

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1. Introduction

In today's world, radioactivity is utilized across various applications, with nuclear medicine and energy production being the industries managing the highest activities levels. The use of alpha and beta-emitting radionuclides in medical diagnosis and therapeutics continues to rise, driven by advancements in producing high-purity, short-lived radionuclides, employing organic ligands, and developing precise measurement devices. Given the often-high activity levels involved, two key concerns arise: assessing the radiation dose received by patients and healthcare professionals, and managing the biological waste from treated patients [1].

Nuclear power plants (NPPs) play a crucial role in global energy production, serving as one of the primary energy sources worldwide. However, their operation carries the potential risks of leaks, accidents, and radioactive discharges, necessitating rigorous monitoring and surveillance of NPPs and related products, including nuclear waste. Once a NPP ceases operation, decommissioning procedures commence to safely dispose all radioactive material, from nuclear fuel to constituent materials. Currently, around 200 NPPs in Europe alone have either surpassed or are nearing the end of their expected lifespans after 30 years of operation. Consequently, decommissioning procedures will become increasingly prevalent among European NPPs in the near future [2,3].

Nuclear medicine and nuclear decommissioning operations generate substantial amounts of liquid and solid materials that require characterization. The analysis of these samples can be highly complex due to the presence of multiple radionuclides, particularly in NPP decommissioning scenarios. In nuclear medicine, urine and blood samples from patients and healthcare professionals must be analysed to assess the radioactive dose received when labeled radiopharmaceuticals are administered [4]. Conversely, in NPP decommissioning, materials such as effluents or building materials must be classified based on their radioactive composition before being treated (if it is required) and disposed of [5,6]. Therefore, there is a need for ultra-fast, selective and pseudo-quantitative analytical strategies. These methods can significantly enhance the characterization productivity by reducing costs, analysis time, and the number of samples requiring full individual radionuclide analysis [7,8].

Plastic scintillators (PS) are an effective detection tool that can be used for this purpose. PS can convert the kinetic energy of a radioactive emission into detectable photons. They are easy to prepare, chemically stable, and capable of withstanding aggressive media, such as nuclear waste samples, due to the addition of crosslinkers [9]. Additionally, their surface can be modified by coating them with a selective extractant, making the system selective towards a target radionuclide. This approach, utilizing PS in the form of microspheres coated with an extractant (PSresin) [10–12], has been used successfully to a wide range of radionuclides in two situations: continuous monitoring of effluents and analysis of specific radionuclides through column separation. However, its application for ultra-fast analysis is limited because managing microspheres is not straightforward. It requires reagents manipulation and devices to pass the solution through the PSresin.

This work presents the development of a novel PS in the form of a disk polymerized within a scintillation vial, with an immobilized extractant on the surface (PSkit), enhancing the system selectivity. The PSkit offers the potential for ultra-fast measurement as sample treatment is performed directly on the PSkit, with selectivity facilitated by the chosen extractant. The PSkit has been developed for ^{99}Tc using Aliquat-336® as extractant, a proven efficient extractant for selective analysis with PSresins, which interact with ^{99}Tc , in form of TcO_4 through ion exchange [13,14]. Technetium is of particular interest in both NPP decommissioning (^{99}Tc) and nuclear medicine ($^{99\text{m}}\text{Tc}$). ^{99}Tc , a long-lived (2.11×10^5 years) beta-emitting radionuclide ($E_{\text{max}} = 291$ KeV) is mainly produced by the nuclear fission of ^{235}U or ^{239}Pu in NPP reactors [15–17]. $^{99\text{m}}\text{Tc}$ is a short-lived (6.02 h) gamma emitting radionuclide ($E_{\gamma} = 140$ KeV) is used to assess neuroendocrine or

colorectal tumours as well as bone imaging [18,19].

2. Experimental section

2.1. Reagents

Plastic scintillators (PS) were prepared by polymerizing a mixture containing styrene > 99 % (St) (Acros Organics, Geel, Belgium), divinylbenzene 80 % (DVB) (Merck, Darmstadt, Germany), 2,5-diphenylloxazole scintillation grade (PPO) (Merck), bis(5-phenyl-2-oxazolyl) benzene scintillation grade (POPOP) (Acros Organics), 2,2'-azobis(2-methylpropionitrile) (AIBN) (Fluka-Honeywell, Charlotte, US), and either toluene > 99.7 % (VWR Chemicals) or heptane > 99.0 % (Alfa Aesar, Haverhill, USA). The polymerization was conducted in a 20 mL glass or polyethylene scintillation vial (PerkinElmer, Waltham USA). Before use, St and DVB were purified by passing them through alumina in a syringe with glass wool at the bottom.

PSkits were prepared by coating the PS with Aliquat-336® for synthesis (Alfa Aesar) using methanol > 99.9 % (Merck) as solvent.

Radioactive standards used were: 55.1 (0.5) Bq/g ^{99}Tc (Amersham International, Buckinghamshire, UK); 38.4 (0.5) Bq/g ^{36}Cl (Eckert Ziegler, Berlin, Germany); 52.5 (0.4) Bq/g ^{137}Cs (Orano Lea, Châtillon, France); 38.5 (0.3) Bq/g $^{90}\text{Sr}/^{90}\text{Y}$ and 46.3 (1.4) Bq/g ^{238}Pu (Amersham International); 24.4 (0.7) ^{236}U and 23.8 (0.7) Bq/g ^{230}Th (NIST, Gaithersburg, USA).

Sample treatment and PSkits rinsing was done using the following reagents: hydrochloric fuming acid 37 % (Merck), nitric acid 69 % (Merck) and hydrofluoric acid 48 % (Merck).

Matrices of simulated samples were prepared with sodium chloride > 99.0 % (ITW Reagents Panreac, Castellar del Vallès, Spain), aluminium nitrate nonahydrate for analysis (Merck), sodium hydroxide for analysis (ITW Reagents Panreac) and double deionised water.

Liquid scintillation measurements for yield assessment were performed using OptiPhase HiSafe 3 scintillator cocktail (Perkin Elmer).

2.2. Apparatus

A dry Block heater 3 from IKA® was used for PS polymerization. Scintillation measurements were conducted using a Quantulus 1220 liquid scintillation spectrometer (PerkinElmer). Stable isotopes analysis was performed using an OPTIMA 8300 ICP-OES detector (PerkinElmer) or an ELAN 6000 ICP-MS detector (PerkinElmer). Secondary electron images (SEM) were obtained with a JSM-7100 scanning electron microscope (JEOL, Tokyo, Japan). ICP and SEM were conducted at the Scientific and Technological Centres of the University of Barcelona (CCiTUB).

2.3. Procedures

2.3.1. PS and PSkits synthesis

Two different compositions were used to prepare the PS: 32:1(w/w) and 2:1 (w/w) ratios of St and DVB. In all cases, 1 mL of the monomer and crosslinker mixture was used. The solution also contained 3 % PPO, 0.05 % POPOP and 0.07 % AIBN relative to the total amount of St and DVB solution [20]. The mixture was prepared by weight in a 20 mL glass or polyethylene scintillation vial. The vials were placed in the dry block heater at 70°C for 22 h, then cooled at room temperature. Finally, PS were cleaned with 10 mL of ethanol in an end-over-end mixer for 1 h. PS were prepared in absence or in presence of toluene (0.25, 0.5 and 1 mL) or heptane (0.25, 0.5 and 1 mL) as porogens.

PSkits were prepared by adding 1.5 mL of an extractant solution (1.036 g of Aliquat-336® in 100 mL of Methanol) to each vial containing the PS and evaporating the solvent in the oven at 60°C. To ensure better distribution of the extractant on the PS surface and to form a uniform thin film, additional volumes of methanol (0.5 mL and 0.25 mL methanol) were added consecutively as the solution approached evaporation.

After the final addition, the vials were left to allow complete evaporation.

2.3.2. PS characterization

A 25 μL aliquot of a ^{99}Tc solution (7 Bq) was deposited onto the surface of the PS. The vials were placed in an oven at 40°C . After a 2-hour period, during which the solvent evaporated, the vials with ^{99}Tc dispersed on the surface were measured in the scintillation counter.

2.3.3. PSkits characterization

Characterization of the prepared PSkits was conducted through several experiments. In each case, 10 mL of a ^{99}Tc solution in 0.1 M HCl, an optimal medium for retaining ^{99}Tc in Aliquat-336[®] extractant, was added to the PSkits. After 24 h, the solution was removed and the PSkits were directly measured in the scintillation detector for 1 h. Additionally, 6 mL of the waste solution was mixed with 14 mL of scintillation cocktail in a 20 mL scintillating vial and measured for 1 h to determine the detection efficiency of the PSkits and the retention yield.

Five different contact times were studied: 1 min, 10 min, 30 min, 4 h and 24 h. Three stirring methods were evaluated: gently stirring (moving the PSkit softly for 30 s), vigorous stirring (moving the PSkit quickly up and down for 30 s) and vortex stirring (stirring in a vortex for 1 min at 3000 rpm). After stirring and a 10-minutes contact period, the PSkits were emptied and rinsed twice with a 0.1 M HCl solution, stirring for 30 s and allowing 3 min between each rinsing.

Interference retention was evaluated by exposing the PSkits to 10 mL HCl 0.1 M solution containing various interferents (^{63}Ni , ^{241}Am , ^{90}Sr , ^{36}Cl , ^{137}Cs , ^{238}Pu , ^{236}U and ^{230}Th) for 10 min. The activities of the interferents ranged between 6.7 to 7.7 Bq. After exposure, PSkits were rinsed first with 0.1 M HCl and then with double-deionised water. PSkits were gently stirred for 30 s, allowing 3 min between each rinsing solution.

2.3.4. Analysis of simulated nuclear waste samples

Two distinct matrices were prepared to simulate samples of liquid nuclear waste from Hanford storage tanks: AN106 and AP101. The AN106 matrix comprised a solution of 7 M NaOH, 1.2 M $\text{Al}(\text{NO}_3)_3$ and 0.67 M NaCl, while the AP101 matrix consisted of a solution of 0.457 M NaOH, 0.0667 M $\text{Al}(\text{NO}_3)_3$ and 0.0805 M NaCl. These matrices were then spiked with two different mixtures of radionuclides: Mixture A, containing 1.7 Bq of ^{99}Tc ; 4 Bq of ^{137}Cs and 2.7 Bq of ^{90}Sr and mixture B containing 2.1 Bq each of ^{99}Tc , ^{63}Ni , ^{238}Pu and ^{236}U . Each sample underwent analysis via two procedures: P1 and P2.

Procedure P1 involved adding 1 mL of the sample directly into the PSkit, followed by double deionized water to reach a volume of 10 mL.

Procedure P2 entailed adding 1 mL of the sample to the PSkit. Subsequently, a drop of phenolphthalein was introduced, followed by gradual addition of HCl 5 M drop by drop until the solution turned colourless (ensuring an acidic pH), after which 0.1 M HCl was added to reach a volume of 10 mL.

In both procedures, PSkits were gently stirred for 30 s and exposed to the solution for 10 min. Following exposure, PSkits were rinsed sequentially: first with 10 mL of HCl 0.1 M, then with 10 mL of a solution of 0.1 M HF and 0.1 M HNO_3 , and finally with 10 mL of double deionised water. After each rinsing solution was added, the PSkits were gently stirred for 30 s and left to stand for 3 min. Subsequently, the PSkits were measured in the scintillation detector for 1 h.

2.3.5. Analysis of spiked urine samples

10 mL urine sample collected from an adult male was spiked with ^{99}Tc at two different activity levels (0.06 Bq and 0.33 Bq) and acidified with some drops of 5 M HCl. The solution was added to the PSkit, gently stirred for 30 s and remained in contact for 10 min. Following the exposure, PSkits were rinsed with 0.1 M HCl first and then with double deionised water, following the same procedure as used as for other samples. Finally, the PSkits were measured in the scintillation detector

for 1 h.

2.4. Data treatment

Data obtained from the liquid scintillation detector was processed using MATLAB (Mathwork, Natick, USA). Scintillation spectra were smoothed for better representation using a Savitzky-Golay algorithm with a first-degree polynomial and an average window of 10 points on each side.

Detection efficiency is defined as the net count rate (in counts per minute) measured by the detector divided by the ^{99}Tc activity (in disintegrations per minute) retained in the PSkit or deposited on the PS.

The retention of radionuclides in the PSkit was calculated as the ratio of the activity retained in the PSkit to the total activity added (1). The activity retained in the PSkit was determined by subtracting the activity measured in the waste solution (via liquid scintillation) from the total activity initially added to the PSkit.

$$Ret_{99\text{Tc}} = \frac{{}^{99}\text{Tc, added} - {}^{99}\text{Tc, not retained}}{{}^{99}\text{Tc, added}} \cdot 100 \quad (1)$$

The activity of the simulated waste samples from Hanford and the spiked urine sample was calculated using the following expression (2):

$$Activity(\text{Bq}) = \frac{\text{Count rate}_{\text{sample}}(\text{cpm}) - \text{Count rate}_{\text{background}}(\text{cpm})}{60 \cdot \frac{Eff_{99\text{Tc}}}{100} \cdot \frac{Ret_{99\text{Tc}}}{100}} \quad (2)$$

Detection limits (3) were established using the Curie equation [21].

$$DL = \frac{2.71 + 4.65 \cdot \sqrt{\text{Counts}_{\text{background}}}}{V \cdot t \cdot \frac{Eff_{99\text{Tc}}}{100} \cdot \frac{Ret_{99\text{Tc}}}{100}} \quad (3)$$

where V is the sample volume (in L); and t is the counting time (in seconds).

All experimental related to the development of the PSkits were performed in triplicate. Uncertainty corresponds to the experimental standard deviation with $k = 1$.

For sample measurements, uncertainty ($k = 1$) was calculated taking into account the count rate statistics for 1 h counting time and the experimental standard deviation of the retention and the detection efficiency obtained in standards.

3. Results

The concept of the PSkits as a tool for ultra-fast, selective, and pseudo-quantitative analysis of liquid waste builds on previous experience with plastic scintillators in the form of resins (PSresins) for selective radionuclide analysis. However, significant differences were identified and addressed. Firstly, the PS support was modified to allow a direct manipulation of the sample without need for additional devices. This involved transitioning from micro-sized resins packaged in solid-phase extraction cartridges to a 0.5 mm PS disk with the extractant applied to the surface, fixed in the bottom of a 20 mL liquid scintillation vial. A thin PS disk presents the advantage that the amount of reagents used is small, background will be low and for most of the beta particles emitted, emitted from the surface, its energy will be fully deposited on the PS disk. On the opposite side, the location of the disk at the bottom of the vial will be not the optimum from the point of view of the scintillation detection. For these reasons, this change on the format necessitated optimizing both the preparation and the analytical procedures to achieve ultra-fast analysis, including defining the protocol and optimizing steps such as contact time, stirring and cleaning. Finally, a validation with simulated high-complexity samples, similar to those encountered in NPP decommissioning and nuclear medicine, was required.

3.1. PSKits development

The development of PSKits involves two steps: the preparation of the PS and immobilization of the extractant on its surface. Since a disk of PS has a lower specific surface compared to the same mass of micro-sized PSresins, one of the initial objective was to increase the porosity of the polymer and, consequently, its surface area. Porosity on polymers can be generated by adding a porogen during the polymerization of the monomers. However, these polymers must include a crosslinker to ensure the mechanical integrity and avoid disintegration. Additionally, for PSKits, the polymer must be anchored to the vial (plastic or glass) throughout the sample treatment, which also depends on the structure of the PS.

3.1.1. Study of St-DVB proportions for the PS synthesis

Two proportions of St-DVB (w/w) were studied (32:1 and 2:1), initially without the addition of porogen. PS samples were prepared in glass vials. Table 1 presents the detection efficiency and quenching parameter values for measurements obtained after the complete evaporation of 25 μL of a ^{99}Tc standard solution previously applied to the PS surface.

The detection efficiency values obtained are quite high, considering that the radionuclide is deposited on the surface of the PS, which means some beta radiation could be emitted in opposite direction to the scintillator. These results suggest some penetration into the PS may occur, as detection efficiencies exceed 50 %. Moreover, the results can be considered reproducible as relative standard deviation is of 2 % and 8 %. The SQP(E) values are lower than those typically observed in PS microspheres (around 800) indicating that light transmission is not fully efficient and some quenching effects are happening. The presence of DVB may contribute causing chemical quenching. However, increasing the DVB from 32:1 to 2:1 only causes a slight decrease in the SQP(E) and detection efficiency, suggesting that quenching could also be attributed to other factors, such as optical effect from inefficient light transmission from the PS. The spectra obtained (Fig. 1) follow the same trend, with a shift to lower energies as the DVB proportion increases. Overall, both proportions perform similar (with 32:1 being slightly better) and are suitable for the PSkit preparation.

3.1.2. Study of porogens addition on PS synthesis

Two substances, heptane and toluene, were added to the polymerization mixture as porogen. Since they do not bond with polymer structure, they can be removed through lixiviation with an organic solvent. Three different amounts of porogen (0.25/0.5/1 mL) were evaluated in both PS proportions (32:1 and 2:1).

PS in the 32:1 proportion did not form correctly with any of the porogen amounts studied. This was due to the combination of too much porogen and too little crosslinker, resulting in PS that lacked sufficient mechanical stability and become deformed or shrank.

PS in the 2:1 proportion synthesised with toluene showed some lack of reproducibility in terms of geometry. However, this issue was not observed when using heptane. Additionally, some PS samples did not adhere to the bottom of the glass vial, especially when 1 mL of porogen was used.

PS successfully prepared were assessed using a scanning electron microscope (SEM). A top and cross-sectional view of some of the foils can be seen in Fig. 2.

PS samples prepared with toluene exhibited surface roughness and visible channels in the cross-section. However, there was no clear

Table 1
Detection efficiencies and SQP(E) for 32:1 and 2:1 St:DVB PS.

St:DVB	Efficiency [%]	SQP (E)
32:1	57 (1)	670 (10)
2:1	52 (4)	653 (36)

evidence of pore formation. In contrast, PS samples prepared with heptane revealed several spots on the surface, and the cross-section displayed a different texture compared to those prepared with toluene. This texture appeared more consistent with a conglomeration of polymer, potentially allowing the diffusion of the extractant and/or the sample when applied.

These PS were used to measure ^{99}Tc through drop deposition and subsequent dryness evaporation (Table 2). The detection efficiency increased with the amount of porogen added. Moreover, PS prepared with toluene showed lower detection efficiency compared with heptane. This may be correlated with a higher penetration of the solution into the PS surface, indicating greater porosity, when using heptane and high amount of porogen. Values of relative standard deviation are between 3 % and 12 % which indicate an acceptable reproducibility.

Analysis of the spectra reveals that the spectrum obtained using 1 mL of porogen appears at higher energy levels, correlating with the higher efficiency observed (Fig. 3). No luminescence peak was observed in the spectra, even when the PSkit was measured immediately after preparation. This observation was in accordance with previous experience with PSresin, where only when using very high nitric acid concentration (HNO_3 8 M) luminescence was observed on the first channels (0–200) [10, 11]. Nevertheless, if the measurement is not needed immediately, it is recommended to store the vials in the dark at least 2 h before measurement.

Based on the results, 1 mL of heptane with a 2:1 St-DVB proportion was selected as the optimal porogen. This choice ensures a higher likelihood of the PS adhering to the vial, while also providing higher efficiency and spectra at higher energies levels.

3.1.3. Glass vs plastic vial

Glass and plastic vials were compared directly using the PSKits. Although the 2:1 proportion with heptane shows more promising results, the 32:1 proportion without porogen was also included in the study to examine if crosslinker quantity or porous presence could affect other factors. The synthesis of PS in plastic vials (32:1 and 2:1 proportion with 1 mL of heptane) was successful, with only a slight deformation of the vial due to the heating. The preparation of PSKits by adding a solution of aliquat-336® in methanol and evaporating the solvent was also successful across all formats (type of vial and PS composition).

The PSKits were tested by exposing them to a 10 mL solution of ^{99}Tc in HCl 0.1 M, followed by 3 min shaking in a vortex. After a contact time of 24 h, the PSKits were emptied. Both, the PSkit and the solution were then measured using a scintillation counter to determine the detection efficiency and the retention of ^{99}Tc (Table 3). Notably, some PSKits prepared in glass vials become unglued during shaking, confirming previously observed issues with PS preparation. In contrast, plastic vials remained stable with the PS firmly adhered to the inner surface of the vial.

In all cases retention rates for ^{99}Tc were nearly quantitative, demonstrating that the extractant effectively coats the PS and traps the Tc in the solution.

Detection efficiencies showed significant differences between glass and plastic vials, with higher efficiencies observed for plastic vials. This can be attributed to the greater mechanical stability of the plastic PSKits and also to the better light transmission through the vial walls. This is confirmed by the spectra (Fig. 4) as the glass 32:1 vials presented a two-peak signal with a band at very low energies, indicating poor photon emission quality.

Moreover, plastic PSKits achieved an efficiency above 50 %, as expected from the 2π geometries of the detection device. This higher efficiency could be attributed to the surface roughness of the PS in the plastic vials, which may facilitate the penetration of the extractant in the polymer surface. This might also explain why PSkit with heptane produce better results and more energetic spectrum. In conclusion, plastic vials were selected for the preparation of PSKits.

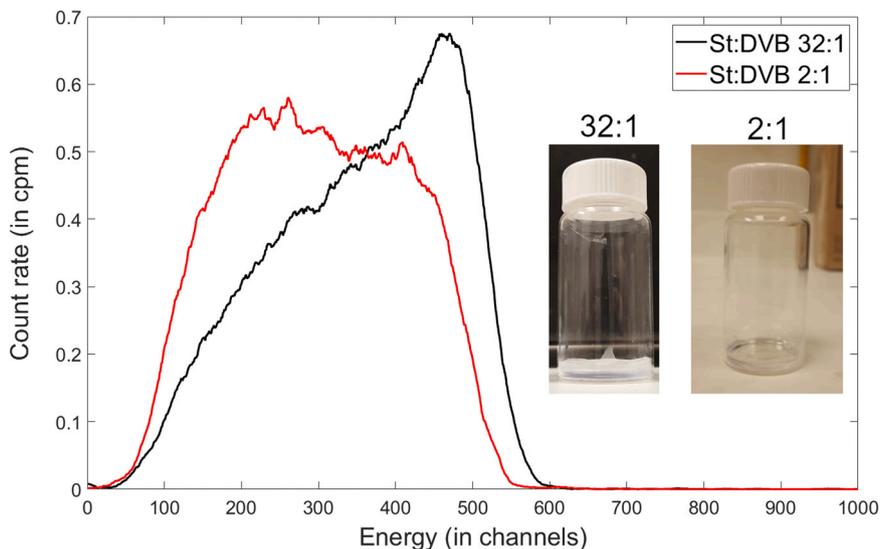


Fig. 1. ⁹⁹Tc Spectrum of 32:1 and 2:1 PSkits.

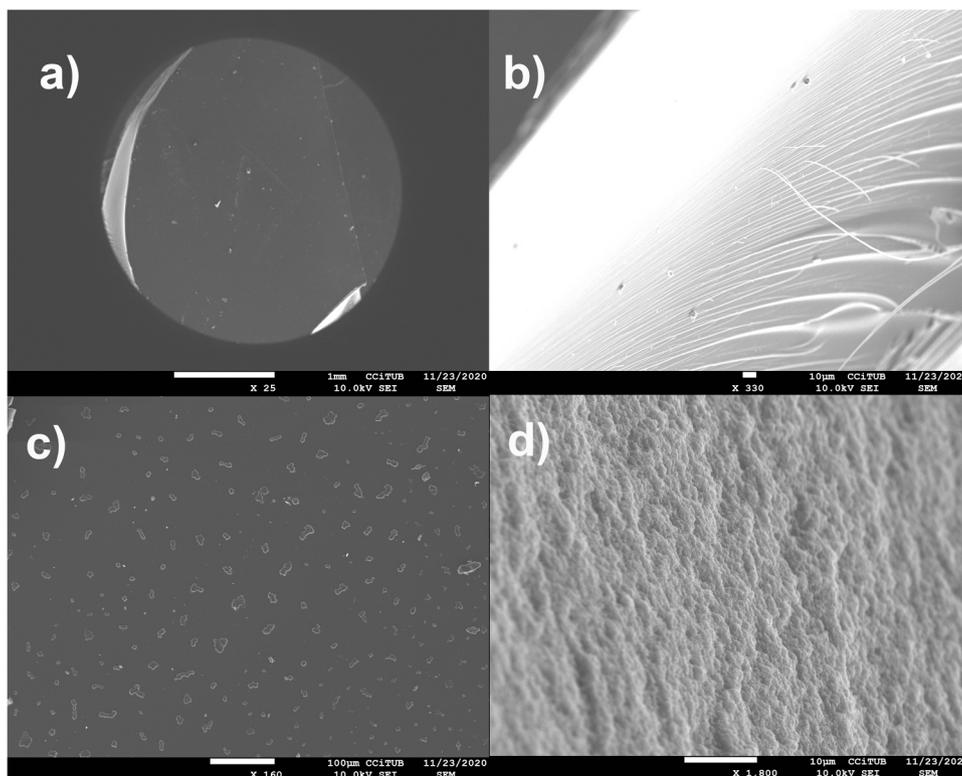


Fig. 2. SEM images of the 2:1 proportion PS: PS-toluene-0.5 (a) surface and b) cross-section) and PS-heptane-1 (a) surface and b) cross-section).

Table 2
⁹⁹Tc detection efficiency and SQP (E) of the 2:1 PS with porogen.

Porogen	Volume	Detection efficiency (%)
Toluene	1	47 (2)
	0.5	41 (5)
	0.25	43 (1)
Heptane	1	52 (1)
	0.5	49 (6)
	0.25	45 (2)

3.2. Analysis method development

With the PSkits configuration established and its capacity for ⁹⁹Tc retention and measurement demonstrated, the usage conditions were explored and optimized. The optimization focused on reducing time, analytical steps, and interference contribution. PSkits used in this evaluation correspond to the 32:1 and 2:1 + 1 mL of heptane St:DVB proportions in plastic vials.

3.2.1. Exposure time optimization

PSkits were designed to quickly, selectively, and semi-quantitatively characterize nuclear waste. The initial 24-hour exposure time used in

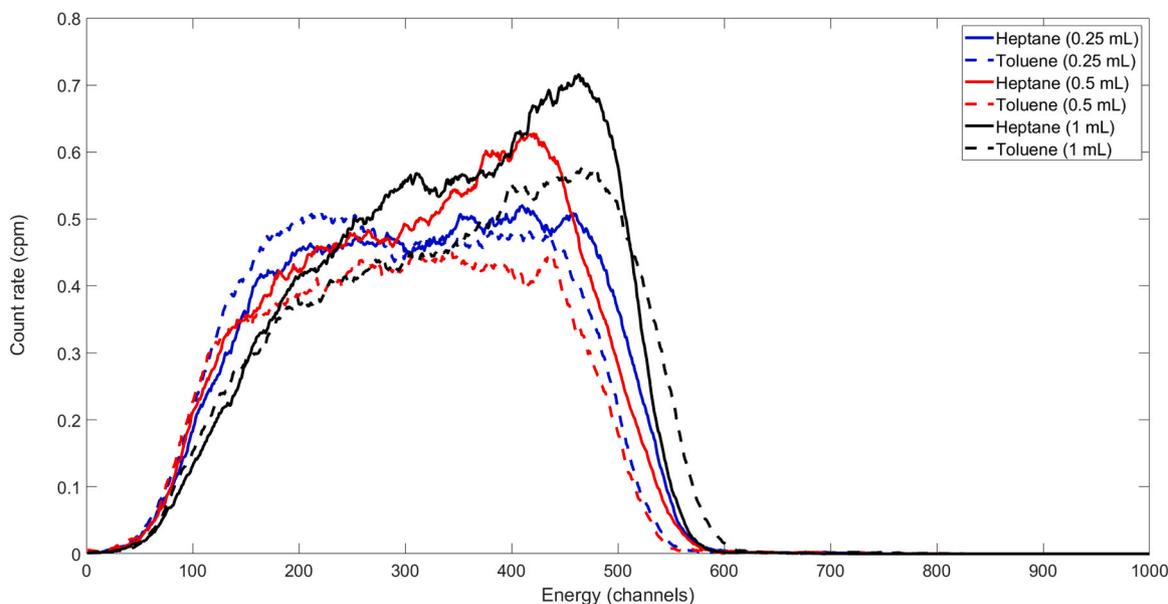


Fig. 3. ⁹⁹Tc spectra with porous PSkits.

Table 3
Detection efficiencies retention glass and plastic PSkits.

Composition	Type of vial	Background (cpm)	Detection efficiency (%)	Retention (%)
32:1	Glass	7.8	20 (2)	98.8 (0.2)
	Plastic	1.1	56 (2)	98 (1)
2:1 with 1 mL heptane	Glass	7.3	42 (10)	>99.5
	Plastic	1.3	65 (3)	97 (1)

scintillation studies is not practical for this purpose. Therefore, exposure times of 1, 10, 30 min, 4, and 24 h were evaluated to determine their impact on detection efficiency and retention rate (Fig. 5).

Retention and detection efficiency clearly increase with contact time, indicating that more time enhances the interaction between the radionuclide and the extractant, allowing it to penetrate in the PS. Variability between replicate measurements also decreases with time,

demonstrating the stability of the extraction and detection process. However, the values obtained at 1, 10, and 30 min are acceptable for pseudo-quantitative detection and, therefore, 30 min was selected as the analysis time, enabling fast analysis while meeting the proposed objective.

3.2.2. Stirring method optimization

The interaction between ⁹⁹Tc in the solution and the PSkits can be enhanced by the exposure time but also through shaking the solution. To evaluate this, three simple shaking methods were compared: gentle stirring with soft circular movements of the vial for 5 min, vigorous vertical shaking of the vial by hand for 1 min, and vortex stirring at 3000 rpm for 1 min. Table 4 show the retention and detection efficiency values obtained when analysing 10 mL solutions containing ⁹⁹Tc.

PSkits measurements were reproducible as low relative standard deviations are obtained, all below 5%. Furthermore, detection efficiencies and retention rates increased in all cases, achieving comparable

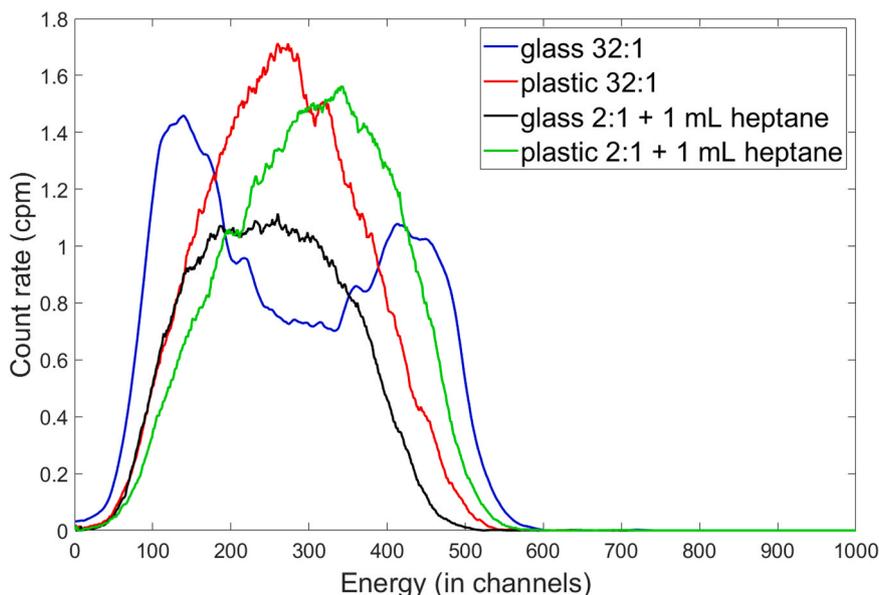


Fig. 4. ⁹⁹Tc PSkit spectra in glass and plastic PSkits.

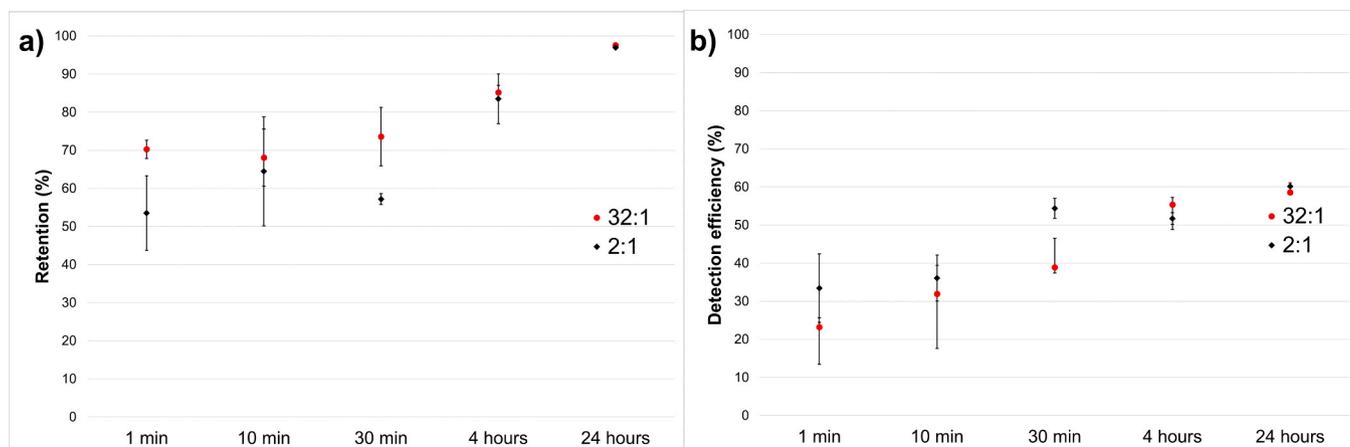


Fig. 5. Variation of the PSkits retention and the detection efficiency for 1, 10, 30 min and 4 and 24 h exposure to ^{99}Tc solution.

Table 4

Comparison of stirring methods. ^{99}Tc retention and detection efficiency after gentle, vigorous or vortex stirring.

PSkit	Stirring Procedure	Retention rate (%)	Detection Efficiency (%)
32:1	Gentle	86 (2)	55 (1)
	Vigorous	77 (3)	50 (0)
	Vortex	91 (2)	55 (2)
2:1	Gentle	85 (2)	49 (2)
	Vigorous	83 (4)	49 (2)
	Vortex	90 (3)	52 (3)

to those achieved with a 24 h contact. Comparing different stirring methods, detection efficiencies and retention rates were observed regardless of the method used. That means that even mild agitation is sufficient to ensure effective interaction between ^{99}Tc and the PSkit, and that the PS and the extractant are well fixed and capable to support a very strong agitation as that of the vortex.

Among the methods studied, gentle stirring was chosen for future experiments due to its simplicity and feasibility for field use, requiring no specialized equipment.

3.2.3. Interferents retention

When analyzing real samples from nuclear facilities, it's common for ^{99}Tc to be mixed with other radionuclides produced during the nuclear fission process. Therefore, it is essential to examine the most frequently encountered radionuclides in these samples to assess their potential impact on the characterization of ^{99}Tc with PSkits. The studied radionuclides included ^{137}Cs , $^{90}\text{Sr}/^{90}\text{Y}$, ^{36}Cl , ^{238}Pu , ^{236}U and ^{230}Th . In this case, after gently stirring the PSkit with the 10 mL solution containing the interfering radionuclide in 0.1 M HCl media, the PSkits were rinsed with 0.1 M HCl followed by double deionized water. The retention rate results are presented in Table 5.

Most of the radionuclides exhibited retentions below 3 % after both rinsing steps, suggesting that they do not significantly interfere with ^{99}Tc measurement. However, ^{238}Pu and ^{230}Th showed partial retention in HCl, which decreased to around 10 % after rinsing with double deionized water. Nevertheless, retention of those radionuclides, as being both alpha emitters, could be detected by spectrum analysis as their signals are characterized by a sharp peak at channel 300 and to get beyond channel 500.

3.3. Sample analysis

3.3.1. Nuclear waste: Hanford site

Validation of the PSkits was conducted through the analysis of complex samples simulating radioactive wastes at the Hanford site. The

Table 5

Interference retention on PSkits after HCl 0.1 M and H_2O double deionised rinses.

Radionuclide	PSkit	Radionuclide retention (%)	
		HCl 0.1 M	H_2O double deionised
^{63}Ni	32:1	n.d.	n.d.
	2:1	n.d.	n.d.
^{241}Am	32:1	n.d.	n.d.
	2:1	n.d.	n.d.
^{137}Cs	32:1	4	3
	2:1	1	1
^{90}Sr	32:1	6	4
	2:1	2	2
^{36}Cl	32:1	3	2
	2:1	3	3
^{238}Pu	32:1	30	17
	2:1	15	7
^{236}U	32:1	4	2
	2:1	1	1
^{230}Th	32:1	11	1
	2:1	11	8

n.d.: non detected

Handford site, operational from 1943 to 1990, was the largest nuclear production complex overseen by the US federal government, primarily focused on the production and processing of plutonium for nuclear weapons industry. Nine nuclear reactors were used to irradiate ^{238}U and generate plutonium. The extraction of plutonium generated radioactive waste that included fission fuel, radioactive byproducts, and the chemicals used in plutonium processing and separation. This radioactive waste, rendered highly alkaline due to addition of NaOH, was stored in 177 tanks with varying chemical and radiochemical compositions. From these tanks, two were selected (AN106 and AP101) as both contain ^{99}Tc and only contain liquid waste (unlike other tanks that also contained sludge)[22–26]. Despite the real waste contained ^{137}Cs and ^{90}Sr at activities several orders of magnitude higher than other radionuclides, the activities of the radionuclides in the two test mixtures (A and B) were kept at the same order of magnitude. Mixture A contained ^{99}Tc , ^{137}Cs and ^{90}Sr (1.7; 4 and 2.7 Bq respectively), while the mixture B ^{99}Tc , ^{63}Ni , ^{238}Pu , and ^{236}U (2.1 Bq of each). Blank samples, containing the same mixtures without ^{99}Tc , were also analysed for comparison.

Samples and blanks were analysed using two procedures (P1 and P2) due to the highly basic nature of the matrices. Count rates on blank samples (without ^{99}Tc) are shown in Fig. 6, compared to the background (1.5 cpm) and the limit of detection (2.3 cpm) for a 1-hour counting period. The values for Mixture A are comparable to matrix blanks and below the LD in all cases (8 of 8 cases). However, mixture B blanks have higher count rates, with 6 out of 8 cases, above the LD, likely due to the

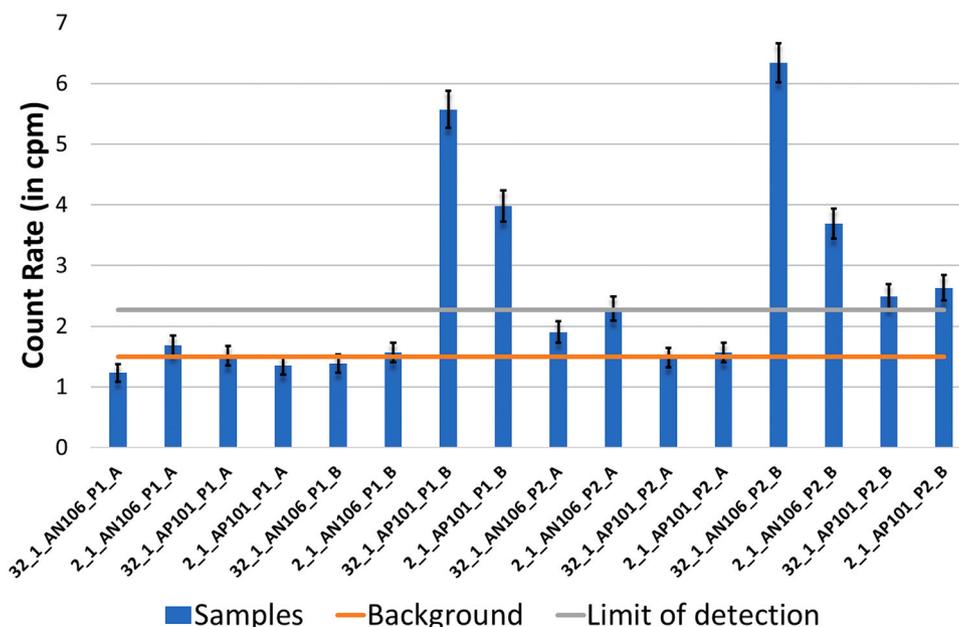


Fig. 6. Background, limit of detection and blank samples count rate (error bars correspond to counting statistics).

presence of ^{238}Pu , which is slightly retained as previously seen. When comparing methods, P1 method provides better results (6 out of 8) than P2 (4 out of 8), probably because the basic medium in P1 do not facilitate the retention of radionuclides in the PSkit.

Quantification errors for ^{99}Tc active samples are shown in Table 6. For this purpose, a constant value of retention and detection efficiency, obtained from standards, was directly applied on the count rate measurement of the PSkit. The values obtained are below 25 % in 80 % of the cases, and all are below 50 % which is acceptable for a pseudo-quantitative method and demonstrate that the method is accurate enough for its purpose. Relative uncertainty associated to each determination ($k = 1$) was around 19 % for 32:1 PSkits and 10 % for 2:1. These values of uncertainty, slightly lower than the errors obtained in the quantification, implies that sample analysis method introduces some uncertainty on the determination. Nevertheless, these differences are acceptable considering the complexity of the samples and the simplicity of the measurement.

Among the analysis methods, P2 provides lower errors in 7 out of 8 cases, likely because the medium of retention in these samples is more similar to that of the calibration standards, making the retention value used more accurate. No significant trend was observed regarding the type of PSkit, sample matrix, or mixture, indicating that quantification is not dependent on these variables.

Spectra obtained for the Handford samples aligned with the typical broad band observed in the ^{99}Tc standards (Fig. 7). This confirmed that the radionuclide measured was ^{99}Tc . The observed deviations likely stems the retention and efficiency values used, which may vary from one sample to another. This variability can be considered acceptable given the sample treatment, measurement method, and the purpose of the

Table 6
Relative errors on nuclear waste sample quantification.

Procedure	PSkit	Sample matrix	Mixture A	Mixture B
P1	32:1	AN106	16	11
		AP101	15	11
	2:1	AN106	-25	3
		AP101	11	3
P2	32:1	AN106	31	18
		AP101	44	12
	2:1	AN106	-36	3
		AP101	-1	18

analysis.

Finally, the limit of detection at different counting times and sample volumes was calculated (Fig. 8). LD values achieved are higher than those required for environmental samples or aliments (few Bq/L) although they are acceptable for determining if exemption values for ^{99}Tc in moderate or bulk materials, 104 Bq/g and 1 Bq/g, are surpassed or not, which was the objective of the methodology.

3.3.2. Urine simulated samples

Given that technetium is also a radionuclide commonly used in nuclear medicine, the application of PSkits was tested by analysing real urine samples spiked with ^{99}Tc . For this analysis, 1 mL of urine spiked with ^{99}Tc was added to the PSkit, followed by 9 mL of HCl 0.1 M to adjust the pH. The shaking and rinsing procedures were identical to those used for nuclear waste samples. As the quantification results showed no differences based on the type of PSkit, the study was performed with the 2:1 proportion with 1 mL of heptane alone.

Firstly, three matrix blanks were measured to confirm that the background registered, 1.6 cpm, was consistent with that obtained with a blank of reagents (1.5 cpm). Subsequently, three urine samples were analysed and quantified using the detection efficiency and retention values obtained with standard solutions. The samples were spiked at two activity levels: the minimum detectable activity (0.07 Bq) and 4 to 5 times the MDA (one sample was analyzed in triplicate at this level). Count rate and relative errors are show in Table 7.

At the low activity level, two of the samples could not be quantified as their count rates were below MDA, while the sample above the MDA was quantified with high but acceptable error. At the high activity level, the samples were quantified with errors below 20 %, indicating that the urine matrix has a minimal effect on the retention (i.e. organic matter) and on the detection efficiency (i.e. colour quenching). This suggest that calibration with HCl 0.1 M is valid. This conclusion is supported by the spectra, which were consistently positioned and had the same shape. .

Moreover, the experimental standard deviation obtained for the sample analysed by triplicate (S1_H), 1.7 Bq (9 % of RSD), was slightly lower that the theoretical uncertainty calculated from the count rate, retention and detection efficiency, 2.2 Bq (12 % or relative uncertainty), confirming that the relative uncertainty of the method is around 10 % ($k = 1$).

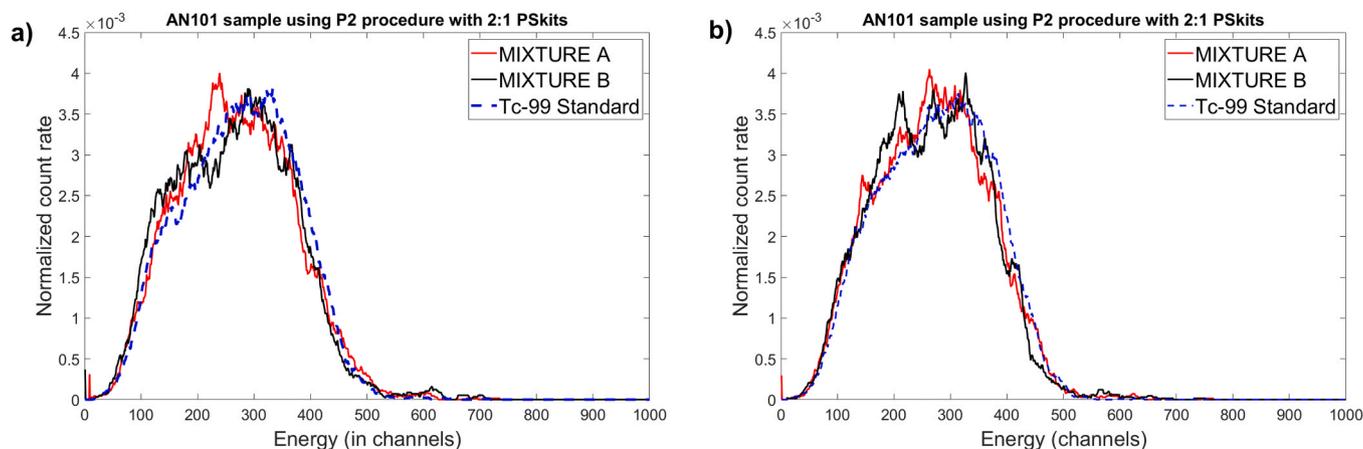


Fig. 7. Normalized spectra of the ⁹⁹Tc samples compared to a standard sample.

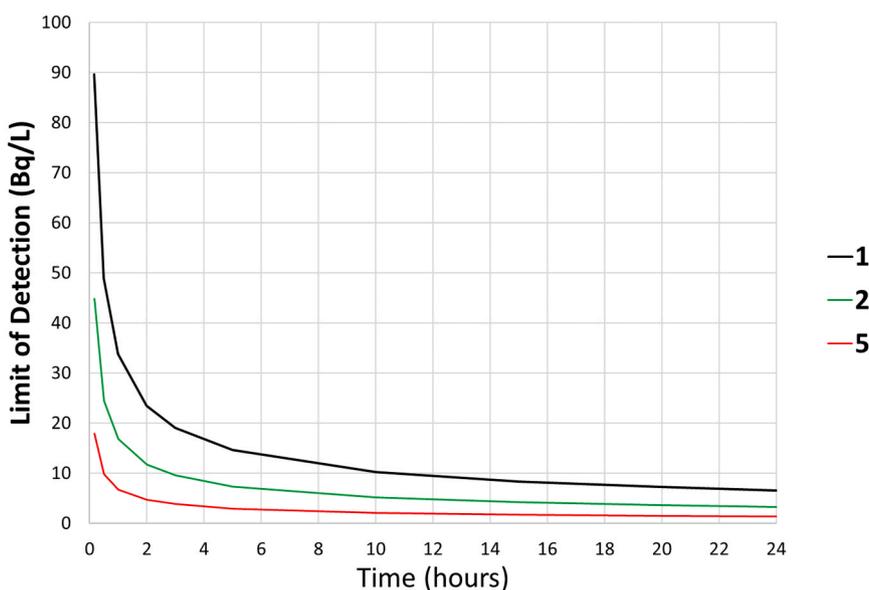


Fig. 8. Limit of detection for the analysis of nuclear waste samples

Table 7
Relative errors on urine sample quantification.

Urine Sample	Activity spiked (Bq)	Count rate (cpm)	Relative error (%)
S1_L	0.069	2.1*	< MDA
S2_L	0.077	2.4	58
S3_L	0.082	2.2*	< MDA
S1_H	0.37	8.2	-3
		7.3	12
		7.2	14
		7.9	6
S2_H	0.35	7.9	6
S3_H	0.34	6.9	19

* Limit of detection was set on 2.3 cpm

4. Conclusion

A novel PS system, named PSkits, for the pseudo-quantitative analysis of ⁹⁹Tc was successfully developed. The development include the design of the PSkit and the procedure of analysis and validation with spiked samples.

Adding a crosslinker during the preparation of the PS slightly decreases the detection efficiency of PSkits but enabled the incorporation

of a porogen. The optimal conditions were found to be the addition of 1 mL of heptane as a porogen to the 2:1 St:DVB proportion, which generated a porous surface. Results obtained with this PSkit were comparable to those with a 32:1 proportion without porogen.

Plastic vials proved to be the best choice for PSkits preparation due to their robustness and higher quality values compared to glass vials. Stirring reduced the analysis time to 30 min while maintaining acceptable retention and detection efficiency values. The optimal method involved gently stirring the vial with soft circular movements for 5 min. Under these conditions, the retention and detection efficiency for ⁹⁹Tc were approximately 80 % and 50 %, respectively.

The PSkit demonstrated good selectivity against common interferences, except for plutonium, with the studied rinsing media.

The analysis of simulated radioactive waste and spiked urine samples using PSkits showed acceptable errors for a pseudo-quantitative method, making it valid for the screening analysis of nuclear waste and urine samples.

Environmental implication

Incorrect characterization of nuclear waste from nuclear power plants (NPP) or hospitals can lead to the spread of radionuclides in the

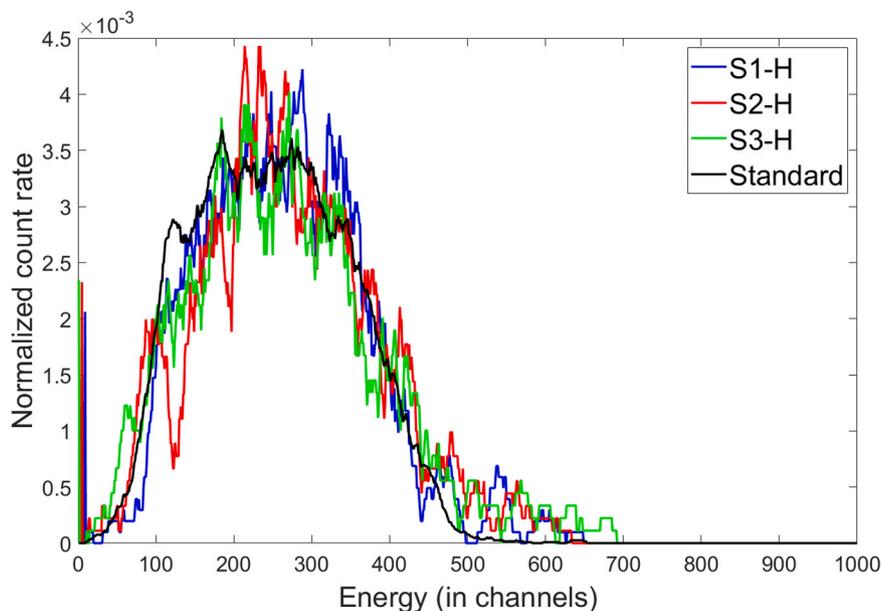


Fig. 9. Normalized count rate spectrum of ^{99}Tc spiked urine sample and HCl 0.1 M standard measured with PSkit.

environment or the improper disposal of non-radioactive materials. Effective waste management and reduction of its environmental impact rely heavily on the ability to accurately and efficiently analyse as many samples as possible. The development of PSkits for the selective and fast characterization of nuclear waste containing ^{99}Tc , a radionuclide of environmental concern due to its high mobility in water, will aid in nuclear waste management and promote environmental protection.

CRedit authorship contribution statement

H. Bagán: Writing – review & editing, Validation, Supervision, Methodology, Conceptualization. **Alex Tarancón:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization. **X. Mendo:** Writing – original draft, Methodology, Investigation. **E. Antoñanzas:** Methodology, Investigation.

Declaration of generative AI and AI-assisted technologies in the writing process

During the preparation of this work the author(s) used ChatGPT in order to improve language and readability. After using this tool/service, the author(s) reviewed and edited the content as needed and take(s) full responsibility for the content of the publication.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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