

Article

Study on Separation of Rhenium, a Surrogate Element of Fissiogenic Technetium, from Aqueous Matrices Using Ion-Selective Extraction Chromatographic Resins

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Abstract: Long-lived fissiogenic technetium, ⁹⁹Tc (half-life, 2.11×10^5 yrs), is a byproduct of the ²³⁵U and ²³⁹Pu fission in nuclear reactors and is a major component in nuclear waste. Hence, the monitoring of ⁹⁹Tc activity in the environmental samples is essential. Techniques used to measure ⁹⁹Tc in environmental samples include radiometric and non-radiometric approaches. Inductively coupled plasma mass spectrometry (ICP-MS) has some advantages among the methods due to its high sample throughput, better selectivity, and commercial availability. Rhenium (Re) is often used as the non-isotopic tracer during ⁹⁹Tc measurement by ICP-MS. From this perspective, studying the separation behavior of Re from the aqueous matrix can provide helpful insight regarding the ecological monitoring of ⁹⁹Tc. In the current work, three extraction chromatographic resins (ECRs), MetaSEP AnaLig Tc-01, MetaSEP AnaLig Tc-02, and Eichrom TRU, have been used to separate Re from the aqueous matrix. Operating variables, such as solution pH, choice of eluent and eluent concentration, matrix cation effect, and retention capacity, have been studied to optimize the separation protocol. The extraction and recovery behavior of Re was used to interpret the selectivity behavior of the ECRs. The Re separation factor at optimized operating conditions comparing with Mo and Ru (interfering elements during the measurement by ICP-MS) for Meta SEP AnaLig Tc-01, Meta SEP AnaLig Tc-02, and Eichrom TRU resin, respectively, are $SF_{Re/Mo} \sim 32$, 16.51, and ∞ (metal not retained at all), while $SF_{Re/Ru} \sim \infty$, 3.25, 5437. In terms of selectivity and retention capacity, MetaSEP AnaLig Tc-01 is the better choice for selective separation of Re, and, assumably so, also Tc, from the aqueous matrices.

Keywords: rhenium; technetium; selective separation; extraction chromatographic resins; aqueous matrix



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1. Introduction

Technetium (Tc), the lightest element in the earth's crust, and it has no stable isotope. Tc-isotopes, ranging from ⁸⁵Tc to ¹¹⁷Tc, are mostly short-lived ($t_{0.5} < 1$ h), except ⁹⁷Tc ($t_{0.5}$, 2.6×10^6 yrs), ⁹⁸Tc ($t_{0.5}$, 4.2×10^6 yrs), and ⁹⁹Tc ($t_{0.5}$, 2.11×10^5 yrs) [1]. The ecological input of ⁹⁷Tc and ⁹⁸Tc is negligible among the long-lived Tc-isotopes from anthropogenic sources. In contrast, ⁹⁹Tc is a thermal fission product of ²³⁵U and ²³⁹Pu that is produced in abundance (fission yield, ~6%) during the operation of nuclear reactors and released into the environment [2,3]. The environmental intrusion of ⁹⁹Tc also occurs from nuclear reprocessing plants, nuclear weapon testing, and the application of ^{99m}Tc in radiopharmaceuticals [4]. The ⁹⁹Tc shows high solubility and low sorption potential at oxidized

and sub-oxic states [5]. In the aqueous system, ^{99}Tc mostly exists as its oxidized form, pertechnetate ion (TcO_4^-), at a wide pH range that migrates at nearly the same velocity as groundwater [6,7]. Due to high mobility, high fission yield, and long half-life, ^{99}Tc is the most crucial fissiogenic Tc for environmental radioactivity safety assessment, nuclear facilities decommissioning, and nuclear waste management.

Both radiometric, e.g., gas flow Geiger-Müller (GM) counter, liquid scintillation counter (LSC), and mass spectrometric techniques, e.g., thermal ionization mass spectrometry, accelerator mass spectrometry, and inductively coupled plasma mass spectrometry (ICP-MS), have been used for the measurements of ^{99}Tc [8–16]. However, radiometric methods are difficult to apply during emergency responses for quantification of trace ^{99}Tc due to relatively long counting time (e.g., GM counter) or high detection limit (e.g., LSC) [1]. In contrast, ICP-MS has advantages over other techniques due to its high sample throughput, commercial availability, high selectivity, and sensitivity. Therefore, ICP-MS is preferred over the radiometric methods to measure trace ^{99}Tc in the environmental samples [3,17,18].

As a trace amount of ^{99}Tc is present in the natural environment, separation is mandatory for precise determination with a suitable technique [19]. Different approaches, such as co-precipitation [20,21], solvent extraction [8,22,23], and extraction with chromatographic resins [10,17,19,24–26], have been used for the separation or pre-concentration of ^{99}Tc from different matrices. However, some drawbacks of the conventional approaches (e.g., co-precipitation, solvent extraction) include slow kinetics, low selectivity, secondary waste generation, high sample volume consumption, etc. Hence, extraction chromatographic resins (ECR) were introduced as effective options to overcome limitations. Ion exchange resins (e.g., Dowex 1-X8, Bio-Rad AG MP-1, or Amberlite IRA-400) are frequently used for ^{99}Tc separation from environmental matrices [9,27,28]. Precise quantification of trace ^{99}Tc after separation by ion exchange resins is challenging owing to the hindrance from co-stripped RuO_4^- and MoO_4^{2-} [29]. The ECR is more advantageous than the other ^{99}Tc separation options because it performs by combining both selectivities of solvent extraction and high separation efficiency of chromatography. TEVA, an ECR comprising a quaternary amine adsorbed or fixed on solid support [30], is commonly used to separate or purify ^{99}Tc from environmental matrices [1,10,25]. However, TEVA fails in quantitatively separating Tc and Ru when Ru exists at high concentrations with other elements in the ecological matrices [21]. Besides, quantitative elution of Tc(VII) from the TEVA resin achieved with 12–16 mol L $^{-1}$ HNO_3 [10,21] and elute of such a high acid concentration is unsuitable for direct injection to the analytical measurements, e.g., ICP-MS. AnaLig Tc-02 [11] and Eichrom TRU [17,18] are other ECRs, which have been evaluated for ^{99}Tc separation from aqueous matrices.

In the current work, three ECRs, namely, MetaSEP AnaLig Tc-01 (Tc-01), MetaSEP AnaLig Tc-02 (Tc-02), and Eichrom TRU resin (TRU), have been evaluated for selectivity in ^{99}Tc separation using rhenium (Re) as a surrogate. The Re, a chemical analog of Tc, is frequently used to predict the behavior of fissiogenic Tc in the aqueous environment owing to its existence in same oxidation state (−1 to +7) and being soluble as perrhenate ion (ReO_4^-) as of TcO_4^- [31,32]. Moreover, a similar Eh-pH diagram was observed for Tc and Re, including analogous environmental mobility [33]. The work aims to include optimization of the extraction parameters for the ECRs for the selective separation of Re, which are assumably applicable to the ^{99}Tc , such as retention and recovery behavior and efficiency towards eluents. In addition, the retention capability and breakthrough volume, the effect of competing ions, and reusability of the ECRs have also been studied. Among the studied ECRs, Tc-01 has not been studied before for separating ^{99}Tc from the aqueous matrices. A comparative study among the ECRs at varying operating conditions has also not been reported. Present work provides an idea about the operational parameters that would be preferable for the selective separation of Tc by using Re as a surrogate.

2. Experimental

2.1. Instrumentation

A NexION 2000 ICP-MS (inductively coupled plasma mass spectrometer), plus S10 autosampler (PerkinElmer; Waltham, MA, USA), were used to quantify element contents in the aqueous matrix. The ICP-MS operating variables are reported elsewhere [34,35].

A GL-SPE vacuum manifold (GL Sciences; Tokyo, Japan), plus a CAS-1 air pump (AS ONE; Osaka, Japan), were used to treat samples in the ECRs. A Milli-Q water purification system (Merck KGaA; Darmstadt, Germany) was used to prepare ultrapure water (UPW) for sample dilution or washing.

2.2. Materials

Stock standard solutions (1000 mg L^{-1}) of molybdenum (Mo), ruthenium (Ru), and Re were prepared, respectively, using molybdenum(V) chloride (99.5%; FujiFilm Wako Pure Chemical; Osaka, Japan), ruthenium(III) chloride hydrate ($>99.9\%$; Nacalai Tesque; Kyoto, Japan), and ammonium perrhenate ($>99\%$; Sigma-Aldrich; Burlington, MA) salts. The standard stock solutions were diluted to prepare the working standards of the elements in the range of mg L^{-1} to $\mu\text{g L}^{-1}$ on a weight basis. Nitric acid (HNO_3 ; 60%), hydrochloric acid (HCl; 35%), sulfuric acid (H_2SO_4 ; 96%), and sodium hydroxide (NaOH; 97%) (Nacalai Tesque; Kyoto, Japan) were used for washing reagent preparation, solution pH adjustment, or eluent. The solution acidities at different pHs (pH 1 to 9) and varying molarities were adjusted using concentrated HNO_3 and 0.1 mol L^{-1} NaOH.

Three different ECRs, namely, Tc-01 (containing organic molecules bonded on silica support), Tc-02 (containing organic molecules bonded on polystyrene support) (IBC Advanced Technologies; American Fork, UT, USA), and TRU (containing octyl(phenyl)-*N,N*-diisobutyl carbamoyl-methyl phosphine oxide dissolved in tri-*n*-butyl phosphate) (Eichrom Technologies; Lisle, IL, USA), were used in the current work. A 500 mg fixed-bed particle volume of each ECR was packed to a bed volume of 3 mL in 6 mL polypropylene (PP) syringes.

2.3. Laboratory Wares

Low-density polyethylene reagent bottles (Nalge Nunc International; Rochester, NY, USA), PP Violamo centrifuge tube and PP volumetric flask (AS ONE; Osaka, Japan), PP DigiTUBE (SCP Science; Montreal, QC, Canada), and micropipette tips (Eppendorf; Hamburg, Germany) were used. All laboratory wares were cleaned following a step-wise washing protocol, which involves dipping in the Scat 20X-PF alkaline detergent (Nacalai Tesque, Japan) ($\sim 24 \text{ h}$) plus soaking in 4 mol L^{-1} HCl ($\sim 24 \text{ h}$) with a thorough rinsing with UPW after each of those steps.

2.4. Separation Process

The separation protocol followed by ECRs includes five steps: rinsing, conditioning, sample loading, pre-elution wash, and elution. First, rinsing of ECRs was performed with HNO_3 and UPW. Next, conditioning of ECRs was conducted using solutions of different acidities (pH, 1 to 9; HNO_3 , HCl, or H_2SO_4 , 0.01 to 2 mol L^{-1}). After that, the sample solution was loaded to ECRs at a predetermined flow rate, and the column effluent was collected. Then, a pre-elution wash of ECRs was conducted with solvents of similar solution acidities to that used in the conditioning step. In the final stage, the ‘retained’ analyte in the extraction column was eluted using HNO_3 of appropriate molarities for quantitative recovery of the target analyte. ICP-MS was used to measure the analyte concentrations in feed solution (S_B), column effluent after loading (S_S), pre-elution wash (S_W), and eluent (S_E). Each experiment was carried out in triplicate, and the averaged mean values with uncertainties were reported. The extraction and recovery behavior of the ECRs were calculated using the following equations:

$$\text{Extraction (\%)} = \frac{S_B - S_S - S_W}{S_B} \times 100 \quad (1)$$

$$\text{Recovery (\%)} = \frac{S_E}{S_B - S_S - S_W} \times 100 \quad (2)$$

The sample loading and elution flow rates in ECRs should be low enough to enable efficient retention and recovery, and they should be sufficient enough to avoid prolonged sample processing [36]. Based on the observations on flow rates of similarly packed columns, the allowable flow rates for column experiments should be between 0.1 and 2 mL min^{−1} [34,35]. Therefore, we maintained the flow rate in this experiment at ~0.5 mL min^{−1}.

2.5. Effect of Interfering Ions

In addition to matrix elements, potential interferences from ⁹⁹Ru, ¹⁰⁰Mo, and ⁹⁸Mo may occur during the measurement of ⁹⁹Tc in environmental samples by ICP-MS [10]. Therefore, to investigate ECRs' efficiency in minimizing the impact of interfering elements, a solution containing 250 µg L^{−1} of the target analyte and interfering ions (Ru or Mo) at a molar ratio of 1:1 was treated at the optimal conditions. The efficiency of ECRs in separating the target analyte (Re) from the interfering ions was explained using the term separation factor (SF). The SF denotes the distribution ratio of Re (D_{Re}) to that of other metals (D_M) in the ECRs solid phase and mobile solution phase after loading of feed solutions of varying acidities [37], which is computed using the following equation:

$$SF_{Re/M} = \frac{D_{Re}}{D_M} \quad (3)$$

2.6. Adsorption Capacity and Breakthrough Volume

The adsorption capacity of the ECRs, conditioned at pH < 2, was determined by loading 100 mL of Re (C_{Re} , ~100 µg mL^{−1}; matrix, H₂O)~0.08 mg mL^{−1}; matrix, H₂O) solution of pre-optimized acidities at 25 °C by sequential loading of 4 mL at each step. The C_{Re} of solutions before and after the loading was measured in ICP-MS. Adsorption capacity (Q , mg g^{−1}) of the ECRs at varying solution feed volume (mL) was computed using the following equation (W , mass of ECRs in g; V , solution volume in L as passed through the ECRs; C_i and C_f , initial and final C_{Re} in mg L^{−1}):

$$Q = \frac{(C_i - C_f) \times V}{W} \quad (4)$$

The breakthrough volume (V_B) of ECRs was determined by continual loading of acidity-regulated solution (C_{Re} , 100 µg mL^{−1}) until some of the analytes began to appear in the S_S , i.e., the ECR sorbent reached the ion retaining capacity. The breakthrough curve was obtained by plotting the analyte concentrations in the loading solution against the sample volume passed through the sorbent.

3. Results and Discussion

3.1. Effect of Solution pH

Solution acidity significantly impacts metal retention in ECRs [36]. The Re extraction rates (as ReO_4^-) in the ECRs at varying solution acidities (pHs, 1 to 9; acid concentrations, 1 and 2 mol L^{−1} HNO₃) are shown in Figure 1. Tc-01 demonstrated quantitative retention of Re (≥99%) at pHs 1 to 9. The uniform retention of Re at Tc-01, irrespective of the solution pH, might be attributable to a non-ionizable organic ligand in the ECR sorbent [36]. TRU showed quantitative retention of Re (≥99%) at pHs 1 and 2, whereas the highest extraction of Re at Tc-02 was noted at pH 4 (~95%).

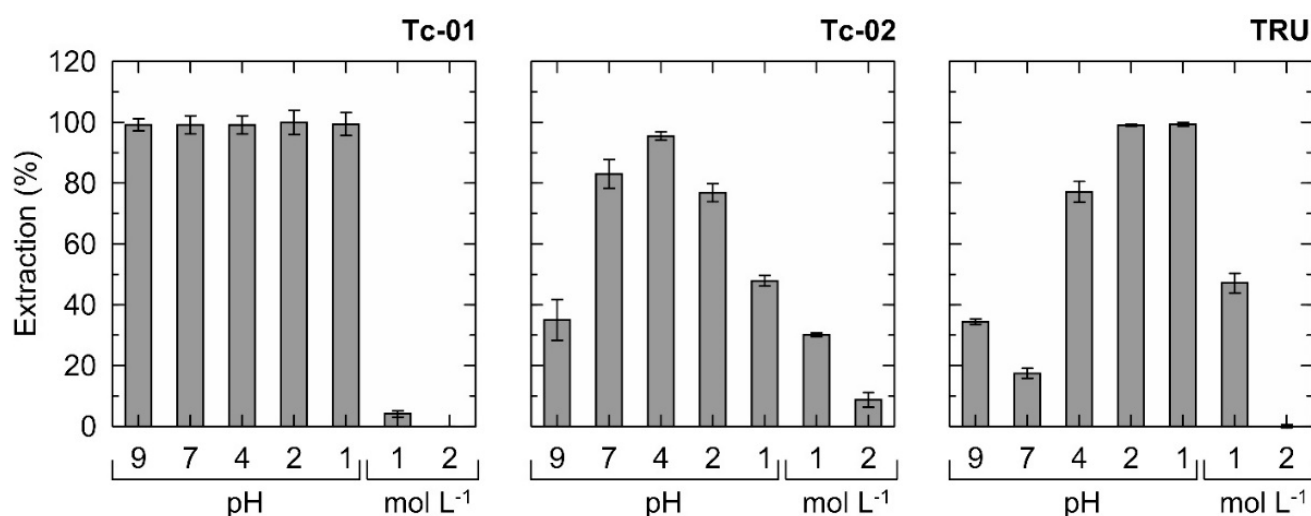


Figure 1. Effect of solution acidities on the Re extraction in the ECRs. Feed solution volume, 4 mL; C_{Re} , 250 $\mu\text{g L}^{-1}$; solution pHs, 1 to 9; acid concentrations, 1 and 2 mol L⁻¹ HNO₃; sample loading flow-rates, 0.5 mL min⁻¹; $n = 3$.

All the ECRs showed insignificant Re extraction at pH < 1. At a high acid concentration in the solution, TcO_4^- combines with H^+ or H_3O^+ to form neutral molecular HTcO_4 or $\text{HTcO}_4(\text{H}_2\text{O})$ [1,38]. The same phenomenon might have led to a decreased concentration of ReO_4^- anions in solution, causing a low retention of Re in the Tc-02 or TRU at low solution pHs.

3.2. Choice of Eluent and Eluent Concentration

During recovery, the eluent should have the property to extract the analyte from the column without affecting the quantitative determination of analytes [39]. In this experiment, ultrapure water (UPW), boiling water (BW), and HNO₃ of different molarity were used as eluents for quantitative Re recovery from the ECRs at optimum conditions (Figure 2). A quantitative elution of Re was observed with 3 mol L⁻¹ HNO₃ from all the ECRs, while BW and 2 mol L⁻¹ HNO₃ can also be used as eluents with TRU. However, UPW and HNO₃ of low molar concentration were unsuitable eluents for Re recovery.

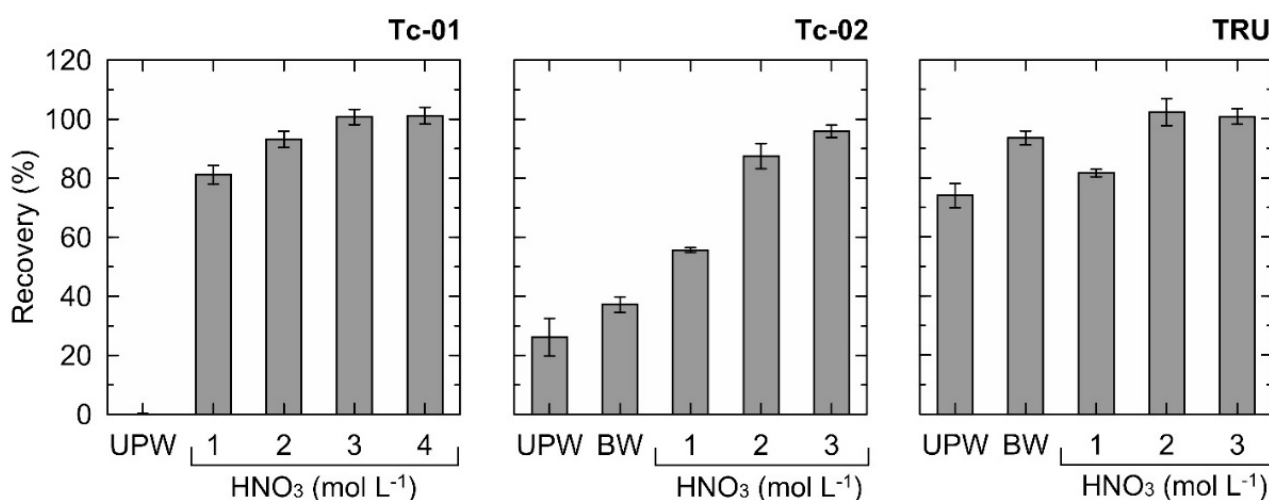


Figure 2. Effect of eluent variants (UPW, ultrapure water; BW, boiling water; HNO₃ of varying molar concentrations) on the Re recovery from the ECRs. Feed solution volume, 4 mL (Tc-01, pH 1; Tc-02, pH 4; TRU, pH 2); C_{Re} , 250 $\mu\text{g L}^{-1}$; eluent volume, 4 mL (UPW, BW, 1 to 4 mol L⁻¹ HNO₃); sample loading and elution flow rates, 0.5 mL min⁻¹; $n = 3$.

We assumed that the component of the extraction resins used in the current work is made of strong base anion exchange resin, and NO_3^- (HNO_3) has a strong tendency to adsorb with such a resin that would result in a decrease in the retention probability of ReO_4^- . In addition, NO_3^- is considered a more acceptable matrix for analytical instruments [40]. Therefore, HNO_3 is the only solvent evaluated to check the recovery as an eluent.

3.3. Effects of Interfering Ions

Mo and Ru create molecular and isobaric interferences during ^{99}Tc measurement in ICP-MS. Hence, the capability of the ECRs in selectively isolating Re from Mo and Ru has been evaluated (Table 1). The SF values indicated that Tc-01 considerably ignores Mo at pH 1 during the retention of Re, whereas Ru is not retained at all at pH 1 to 9. Furthermore, TRU largely dismisses both Mo and Ru at pHs 1 and 2. In contrast, Tc-02 showed poor selectivity towards Re in the presence of Mo and Ru in solution (pH, 4; $\text{SF}_{\text{Re/Mo}}$: 16.51; $\text{SF}_{\text{Re/Ru}}$: 3.25).

Table 1. Separation factor (SF) of Re vis-à-vis competing ions (Mo or Ru).

ECRs	pH	$\text{SF}_{\text{Re/Mo}}$	$\text{SF}_{\text{Re/Ru}}$
Tc-01	1	32	*
	2	0	*
	4	0.83	*
	7	0.95	*
	9	1.15	*
Tc-02	1	4.94	19.90
	2	7.89	61.24
	4	16.51	3.25
	7	20.21	1.25
	9	7.41	0.10
TRU (mol L^{-1})	1	9461	*
	2	*	5437

*: Retention is below the detectable limit, i.e., a significantly high separation factor.

Only a limited number of research has been conducted [11,18,27,31], which reported Re separation using extraction resin. However, the information in those works was insufficient to calculate the SF of Re compared with other elements.

3.4. Retention Capacity and Breakthrough Volume

The analyte concentration and breakthrough volume (the volume of the sample that causes the analyte of interest to be eluted from the column) was used to determine the retention capacity of the ECR sorbent [41]. The retention capacity was measured using a solution containing 0.08 mg mL^{-1} Re at the optimum operating conditions for each ECR (Tc-01, pH 1; Tc-02, pH 4; TRU, pH 2) (Figure 3). The calculated retention capacities were as follows: Tc-01, $3.02 \pm 0.07 \text{ mg g}^{-1}$; Tc-02, $3.61 \pm 0.03 \text{ mg g}^{-1}$; TRU, $1.19 \pm 0.01 \text{ mg g}^{-1}$. The breakthrough volume was computed from the breakthrough curve (analyte concentration vs. feed volume), and the breakthrough occurred after 36, 56, and 12 mL of sample loading, respectively, in Tc-01, Tc-02, and TRU (Figure 3).

3.5. Reusability of the ECRs

The stability and potential recyclability of the column (after cleaning with proper solvent) were examined by several loading and elution operations. The operating capacity was calculated from the loading and elution results at optimum conditions. The result showed that the column was relatively stable up to at least 50 extraction-elution cycles without any significant change in recoveries.

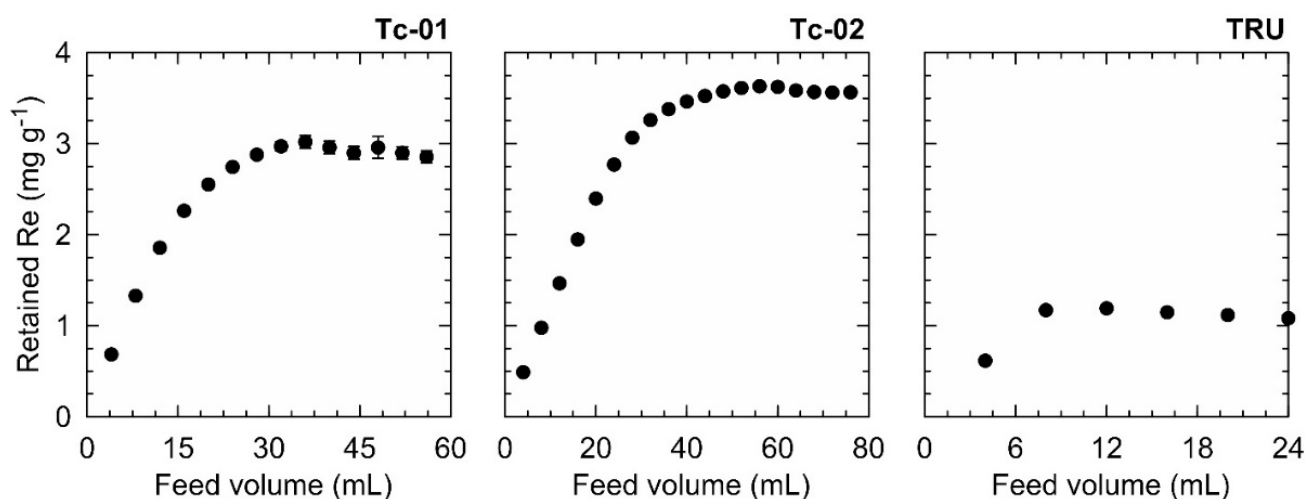


Figure 3. Re retention capacities of the ECRs (Feed solution volume, ~100 mL; C_{Re} , 0.08 mg mL⁻¹; solution acidities: Tc-01, pH 1; Tc-02, pH 4; TRU, pH 2); loading flow-rate: 0.5 mL min⁻¹; $n = 3$).

3.6. Analytical Characteristics

Aqueous solutions containing Re, Mo, and Ru were treated with Tc-01, Tc-02, and TRU ECRs, and the analyte contents in solutions were quantified using ICP-MS. The linear calibration curve was 0.01–1.5 µg L⁻¹ Re, Mo, Ru. The method detection limits, calculated as three times the standard deviation ($n = 10$) of the blank, were 0.0019, 0.0009, 0.0017 µg L⁻¹ Re, Mo, Ru, respectively. The method's precision was also investigated by analyzing 10 replicates of samples containing 5 µg L⁻¹ Re, Mo, and Ru, and the relative standard deviations were 1.7, 3.8, and 1.4% for Re, Mo, and Ru, respectively.

3.7. Optimized Separation Protocol

The optimized separation protocol was designed using 8 mL of aqueous matrix spiked with 250 µg mL⁻¹ Re. The solution acidity of the sample matrix was adjusted for each ECR (Tc-01, pH 1; Tc-02, pH 4; TRU, pH 2). The ECRs were conditioned with buffer solutions of different pHs: Tc-01, pH 1; Tc-02, pH 4; TRU, pH 2 (loading flow rates: 1 mL min⁻¹). The acidity-adjusted sample matrix (4 mL) was loaded in pH-conditioned ECRs (loading flow rates: 0.5 mL min⁻¹). After the sample loading step, washing solutions of specific pH similar to the conditioning step were passed through each ECR (loading flow rates: 0.5 mL min⁻¹). Finally, the retained analyte was back-extracted from the ECR using a suitable eluent (Tc-01 and Tc-02, 3 mol L⁻¹ HNO₃; TRU, 2 mol L⁻¹ HNO₃; elution flow rates: 0.5 mL min⁻¹).

3.8. Application of the Separation Method

The optimized separation protocol was applied for method validation by treating 'real' water samples (pond and tap water) (Table 2). Two pond water samples from *Suzuuchi* (37,024.950' N, 140,058.791' E) and *Inkyozaka* (37,025.499' N, 141,001.05' E), located within the 10 km zone of the Fukushima Daiichi Nuclear Power Plant, as well as tap water sample from our laboratory at Fukushima University, were used. The re-retention rates from spiked samples were ≥89%.

Table 2. Validation of Re-separation protocols with ECRs at optimized conditions.

Sample	Element	Spiked Content (µg L ⁻¹)	Extraction Rates (%)		
			Tc-01	Tc-02	TRU
<i>Suzuuchi</i>	Re	100	89.02 ± 7.80	97.81 ± 0.38	91.24 ± 0.25
<i>Inkyozaka</i>			98.91 ± 0.79	99.05 ± 1.55	99.54 ± 0.41
Tap water			93.28 ± 3.54	99.68 ± 0.60	93.90 ± 0.32

4. Conclusions

Three ECRs (Tc-01, Tc-02, and TRU) were evaluated for selective fissiogenic Tc separation from aqueous matrices using its chemical analog Re as a surrogate. All the ECRs showed a selective retaining capacity of ReO_4^- , minimizing the interfering impacts of RuO_4^- and MoO_4^{2-} , and, assumably, the same will be observed for TcO_4^- . The optimized conditions were as follows: (a) conditioning, washing, and sample solution pHs (Tc-01, pH 1; Tc-02, pH 4; TRU, pH 2); (b) flow rates (conditioning, 1 mL min^{-1} ; sample loading, washing, and elution, 0.5 mL min^{-1}); (c) elution (Tc-01 and Tc-02, $3 \text{ mol L}^{-1} \text{ HNO}_3$; TRU, $2 \text{ mol L}^{-1} \text{ HNO}_3$). It was also observed that the eluent used for the studied ECRs is not as corrosive as the eluent used with commonly used TEVA resin. The Re extraction with Tc-01 worked at a wide pH range, while it was limited with Tc-02 and TRU. TRU has the lowest Re retention capacity, followed by Tc-01 and Tc-02. Overall, Tc-01 will be better compatible ECR for Re separation, and so also for Tc, among the evaluated options, and it can be used for ecological monitoring of ^{99}Tc .

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