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Exploring the reduction mechanism of ⁹⁹Tc(VII) in NaClO₄: A spectro-electrochemical approach

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15 ABSTRACT

Technetium (Tc) is an environmentally relevant radioactive contaminant whose migration is limited 16 17 when Tc(VII) is reduced to Tc(IV). However, its reaction mechanisms are not well understood yet. We 18 have combined electrochemistry, spectroscopy, and microscopy (cyclic voltammetry, rotating disk 19 electrode, X-ray photoelectron spectroscopy, Raman and scanning electron microscopy) to study Tc(VII) 20 reduction in non-complexing media: 0.5 mM KTcO₄ in 2 M NaClO₄ in the pH from 2.0 to 10.0. At pH 21 2.0, Tc(VII) first gains 2.3 ± 0.3 electrons, following Tc(V) rapidly receives 1.3 ± 0.3 electrons yielding 22 Tc(IV). At pH 4.0-10.0, Tc(IV) is directly obtained by transfer of 3.2 ± 0.3 electrons. The reduction of 23 Tc(VII) produced always a black solid identified as Tc(IV) by Raman and XPS. Our results narrow a 24 significant gap in the fundamental knowledge of Tc aqueous chemistry and are important to understand 25 Tc speciation. They provide basic steps on the way from non-complexing to complex media.

26

28 SYNOPSIS

- 29 The reduction of Tc(VII) to Tc(IV) in non-complexing media depends on pH. At pH 2, Tc(VII) gains
- 30 two electrons and consequently Tc(V) gains an additional electron to become Tc(IV); whereas at pH 4-
- 31 10 Tc(VIII) reduces directly to Tc(IV).



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33 KEYWORDS:

34 Technetium • Raman spectroscopy • X-ray photoelectron spectroscopy • Non-complexing media •
 35 Electrochemistry • Electron transfer

36

37 1. INTRODUCTION

Technetium (Tc, Z=43), discovered by Sagré and Perrier in 1937¹, is the lightest element with no stable isotopes. Among them, the most abundant is ⁹⁹Tc, a β -particle emitter with a long half-life of 2.14×10⁵ years. In the early 60s the application as clinical tracer of the metastable isotope, ^{99m}Tc (halflife of 6.007 h), was first published ² and, since then, it has been used for the imaging of several organs like the brain and the lungs.

43

Technetium might occur naturally within the Earth crust originating from spontaneous fission of ²³⁸U. 44 neutron-induced fission of ²³⁵U, or interactions between molybdenum, ruthenium or niobium and cosmic 45 ravs³. However, the vast majority of the ⁹⁹Tc found on Earth is a result of anthropogenic activity such 46 as nuclear energy production and nuclear weapon testing ^{3,4}, as well as the decay product of ^{99m}Tc used 47 in diagnostics ^{5,6}. In a typical 1 GW nuclear power plant, 21 kg of ⁹⁹Tc (13.2×10¹⁵ Bq) are formed 48 annually as fission product ⁷; the global Tc production in 2007 was estimated to be 15.1×10^3 kg. Taking 49 50 this as a rough average, in 2020 there were approximately 4.71×10^5 kg ⁹⁹Tc, equivalent to 2.963×10^{17} Bg, present on Earth. The majority of Tc waste is still waiting for proper disposal in deep geological 51 52 repositories that, combining engineered (e.g. vitrified waste, buffer and sealing materials, borehole fillings) and geological barriers (host-rock) will isolate the radioactive waste from the (hydro)biosphere
 for up to one million years ⁷.

To ensure a safe storage, it is of outmost importance to understand Tc chemical behavior to assess its 55 migration in water, which is strongly influenced by its aqueous speciation⁸. Under oxidizing conditions 56 57 it occurs as pertechnetate, Tc(VII)O₄⁻, an anion with high water solubility and low to no interaction with geochemical barriers ^{9,10}. Consequently, an ingress of ground water to the repository under oxidizing 58 conditions – as worst case scenario – will trigger the migration of Tc(VII) to the biosphere. There, it 59 could easily get incorporated into the food chain causing health problems to animals and humans ^{3,7,11}. 60 61 Under reducing conditions, Tc(IV) is the most stable oxidation state, which commonly forms a solid, TcO₂, with a low aqueous solubility (log $K_{sp} = 8.17 \pm 0.05^{-12}$). Thus, the reduction of Tc(VII) to Tc(IV) 62 is an effective strategy for technetium immobilization. Recently several Fe(II) minerals have been studied 63 in detail: Iron sulfide in the form of pyrite and marcasite ^{13–15} chukanovite, ¹⁶ magnetite ^{17,18}, or other 64 common systems like layered double hydroxides ¹⁹ trigger Tc(VII) reduction and then incorporate, 65 precipitate or adsorb Tc(IV). 66

Despite the clear relevance of the reduction of Tc(VII) from an environmental and chemical point of 67 view, more than 80 years after the discovery of technetium, its reduction mechanisms in water are not 68 69 well understood vet 20 . Although several studies have been performed, especially in acidic media $^{21-23}$, it 70 is not clear whether it proceeds in a direct three-electron transfer or if there are intermediary oxidation 71 states involved ^{24–26}. Moreover, there is no systematic study of the effect of pH and ionic strength on the mechanism. There are also some contradictions observed in the literature. For example, Salaria et al.^{27,28} 72 73 propose the reduction from Tc(VII) to Tc(III) passing through Tc(IV), whereas Grassi et al.²⁹ propose 74 the reduction from Tc(VII) to Tc(IV) with the direct transfer of three electrons, and other authors suggest that the final product would be Tc(IV) with Tc(V) as an intermediary step ^{30–32}. Moreover, it must be 75 76 noted that all these previous studies use ions like Cl⁻ as background electrolytes that are well known to form complexes with technetium 12,33, invalidating such results for a formulation of redox mechanisms 77 78 in pure water. This seriously hampers the modeling of technetium migration behavior in any 79 compartment of geosphere or ecosphere.

80

In order to narrow this substantial gap in the understanding of technetium aqueous chemistry, we studied the reduction of Tc(VII) in sodium perchlorate (NaClO₄), a stable background electrolyte that does not form complexes with Tc(VII) ¹² and, in consequence, minimizes artefacts in reactive transport models for Tc in aqueous media. This will provide valuable reference data for more complex systems in the future. Experiments were performed at $2.0 \le pH \le 10.0$ in order to determine the effect of pH on the mechanism and the reaction products. To get comprehensive molecular understanding on the Tc reduction chemistry, we combined electrochemical (cyclic voltammetry and rotating disk electrode), spectroscopic (Raman and X-ray photoelectron spectroscopy), and microscopic (scanning electron microscopy) methods.

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- 91

92 2. MATERIALS AND METHODS

93 **2.1 Sample preparation**

Radiation safety. ⁹⁹Tc is a β-particle emitter and should be handled only in a dedicated radiochemistry
laboratory with specific radiation safety measurements in place.

96 All solutions were prepared using K⁹⁹TcO₄ (Institute of Radiopharmaceutical Cancer Research at 97 Helmholtz-Zentrum Dresden-Rossendorf), NaClO₄×H₂O (purity \geq 98%, PanReac AppliChem ITW 98 Reagents) and Milli-Q water (resistivity of 18.2 MΩ cm, Water Purified®). In general, 7 mL of 0.5 mM 99 KTcO₄ solutions were prepared in 2 M NaClO₄ at pH 2.0, 4.0, 6.0, 8.0, 10.0. The concentrations of both 100 NaClO₄ and KTcO₄ were constant throughout the experiments. The pH was adjusted by adding small 101 amounts (less than 10 µL in total) of HClO4 or NaOH, changes in ionic strength and viscosity were 102 negligible. The pH was measured using a pH meter (pH3110, WTW) with a pH electrode (SI Analytics 103 Blue Line) calibrated with standard pH buffers 4.006, 6.865 and 9.180 (WTW).

104

105 **2.2** Cyclic voltammetry (CV) and rotating disk electrode (RDE)

106 The CV and RDE experiments were performed in an 884 Professional VA instrument from Metrohm 107 using a three-electrode set-up consisting in a glassy carbon electrode (diameter: 2 ± 0.1 mm) as working 108 electrode (WE), platinum as counter electrode (CE) and an Ag/AgCl (3 M KCl) reference electrode (RE); 109 all potentials where converted to reversible hydrogen electrode (RHE). The electrochemical surface area 110 of the working electrode was determined as 0.035 ± 0.001 cm² with a Randles-Sevcik analysis of 10 mM K₃Fe(CN)₆ in 1.0 M KNO₃ using the diffusion coefficients reported on reference ³⁴. The glassy carbon 111 112 electrode was used in stationary mode for CV and in hydrodynamic mode for RDE. The experiments were performed under normal atmosphere at 25°C and all the solutions were purged with N₂ for 20 113 114 minutes before the measurement. The data obtained with the RDE were processed with the software 115 AfterMath (version 1.5.9888, Pine Research) in order to obtain the limiting currents at the different 116 angular velocities.

118 **2.3 Spectro-electrochemical analysis**

119 Figure S1 in the Supporting Information presents the in-house-built spectro-electrochemical cell. The 120 cell was placed inside a glovebox (GS Glovebox-System GS050912; < 1 ppm O₂) represented by the 121 orange-colored line in the Figure S1a. The cell holder was printed with a 3D printer (3DWOX 1, Sindoh). 122 The quartz cell had the following outer dimensions: width $20 \times \text{depth } 10 \times \text{height } 30 \text{ mm}$ and an optical 123 path length of 5 mm. For the electrochemical reduction of Tc(VII) a three-electrode arrangement was 124 used. The WE was a glassy carbon rod (ALS Japan), the CE was a Pt wire (ALS Japan) and the RE was 125 Ag/AgCl (3 M KCl) (ALS Japan). The electrodes were connected to a potentiostat (PGSTAT 101, 126 Metrohm) outside the glovebox. An UV-vis spectrometer (AvaSpec-ULS2048 StarLine, Avantes) was 127 located outside the glovebox along with the lamp (AvaLight-DH-S-BAL, Avantes) and both of them 128 were connected to the cell holder using optical fiber.

129 The spectro-electrochemical experiments were carried out at 21° C. As general procedure, the sample 130 was placed inside the cell and it was stirred throughout the entire experiment with a 5 mm magnetic 131 stirrer. A potential staircase was applied varying the potential 0.01 V every four minutes (for example: 132 -0.480 V for four minutes, then -0.490 V again for four minutes and so forth until -1 V vs Ag/AgCl or 133 -0.790 V vs RHE). The starting potential of the staircase was -0.490 V vs Ag/AgCl at pH 2.0 and -0.620 134 V vs Ag/AgCl at pH 10.0. In parallel to the potential staircase, UV-vis spectra were continuously 135 recorded (one spectrum every 30 seconds, i.e. 8 spectra per potential value) in the range from 200 to 136 1100 nm. The integration time was 10 ms and a background subtraction was performed using blanks of 137 2 M NaClO₄ at pH 2.0 and 10.0 depending on the sample. The 8 spectra obtained for each potential step 138 were averaged in order to reduce the noise.

139 **2.4 Solid analysis**

140 After the complete reduction of Tc(VII) in the spectro-electrochemical cell at pH 2.0, a black solid was 141 accumulated on the working electrode. The electrode was taken outside the solution and, when it got dry, 142 the solid detached itself immediately and was collected for further study. The reduction in the spectro-143 electrochemical cell was repeated at pH 10.0 obtaining again a solid accumulated on the electrode that 144 was also harvested. Both solid samples were studied by Raman microscopy, with a second batch of the 145 solid obtained at pH 2.0 also being analyzed using scanning electron microscopy with energy dispersive 146 X-ray spectroscopy (SEM-EDX) and X-ray photoelectron spectroscopy (XPS). Experimental conditions for Raman measurements ³⁵ and for SEM-EDX and XPS ¹⁵ are described elsewhere and detailed in the 147 148 supporting information.

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150

153 **3. RESULTS AND DISCUSSION**

154

155 **3.1 Electrochemical Characterization, Cyclic Voltammetry (CV) and Rotating Disk Electrode** (RDE)

321000 Bq remained in the solution, meaning that all Tc(VII) was reduced to the black Tc solid.

The supernatant was analyzed by liquid scintillation counting (1414 LSC Winspectral α/β Wallac, Perkin

Elmer; detection limit: 25 cpm. Measuring time: 10 minutes) finding that only 80 Bq out of the initial

Figure 1 shows the cyclic voltammograms of NaClO₄ solutions in absence (Figure 1a) and presence of
Tc (Figure 1b) in the pH range from 2.0 to 10.0.



159

Figure 1. Cyclic voltammograms at 0.01 V s⁻¹ scan rate in 2 M NaClO₄ under N₂ at different pH values a) in absence of Tc and b) in presence of 0.5 mM KTcO₄. Grey arrows represent the voltage scan direction of the cathodic scan (CS) and the anodic scan (AS).

As mentioned before, unlike chloride (Cl⁻), perchlorate (ClO₄⁻) does not form complexes with technetium ¹². In addition to that, the voltammogram of NaClO₄ (Figure 1a) shows only very small peaks close to 0.1 V vs. reversible hydrogen electrode (RHE) and some hydrogen evolution reaction potentials below -0.625 V at pH 2.0. In the presence of Tc, the voltammograms clearly change. Thus, the peaks in Figure 1b indicate the course of different oxidation states of technetium within the cycling voltammograms.

1.5

Two different Tc reduction behaviors can be spotted in the CVs depending on the pH in the cathodic scan. At pH 2.0 the system clearly shows two peaks during the reduction. A small peak at -0.318 V suggests the formation of an intermediary oxidation state, followed by a second reduction peak observed at -0.424 V. In contrast, at pH 4.0-10.0 one single cathodic peak at -0.560 V indicates a direct Tc(VII) reduction.

174

The voltammograms in Figure 1b show two anodic peaks despite the pH value, i.e. the formation of two
Tc oxidation states. The potential of the reactions depends on the pH alike the reduction: while at pH 4.0
- 10.0 they behave in a similar way (anodic peaks at 0.129 V and 0.570 V), the peaks at pH 2.0 are shifted
to more positive values (0.627 V and 0.789 V).

179

Although, the CVs provide already an idea on the mechanism of the Tc reduction and oxidation, they cannot be used for the determination of the exact amount of electrons transferred, due to the irreversibility of the process. For an improved understanding of the redox processes occurring, we combine cyclic voltammetry at different scan rates and the rotating disk electrode technique to apply the Randles-Sevcik and Levich equations for electrochemical data analysis. A full description of the equations and how to interpret them is defined as follows.

On one hand, by changing the scan rate of the CV, the peak currents can be analyzed with the Randles-Sevcik equation (Eq. [1]) ^{36,37}. It is assumed that all Tc remains dissolved and there is no precipitation or deposition on the electrode.

189 $I_p = 2.69 \times 10^5 n^{3/2} A c D^{1/2} v^{1/2}$ [1]

where I_p is the peak current (A), n is the number of electrons transferred, A the area of the electrode (cm²), c the analyte concentration (mol cm⁻³), D the diffusion coefficient (cm² s⁻¹), and u the CV scan rate (V s⁻¹). The terms n, A, c and D do not change here and can be grouped along with 2.69×10⁵ in a new term Y. Therefore, Eq. [1] can be rewritten as Eq. [2].

194 When I_p is plotted vs. $u^{1/2}$ (Randles-Sevcik plot) a straight line with slope Y is obtained.

195 $I_p = Y v^{1/2}$ [2]

196 On the other hand, using a rotating disk electrode (RDE) the diffusion coefficients and the number of 197 electrons can be determined. RDE is an experimental technique in which the working electrode rotates on its own axis creating a laminar flow of the solution towards the electrode, improving the mass transport
 ³⁸. Such flow can be controlled by the angular velocity of the electrode and the behavior of the current is
 modelled using the Levich equation (Eq. [3]) ³⁸.

201
$$I_L = (0.620) n F A v^{-1/6} D^{2/3} c \omega^{1/2}$$
 [3]

where I_L is the limiting current (A), which is the mass transport limited current obtained at the different rotation speed, *n* is the number of electrons transferred, *F* the Faraday constant (96 485.3329 C mol⁻¹), A the area of the electrode (cm²), *v* the kinematic viscosity of the electrolyte (cm² s⁻¹), *D* the diffusion coefficient of the species under study, i.e. the electroactive species (cm² s⁻¹), *c* the analyte concentration (mol cm⁻³) and ω the angular velocity of the RDE (rads⁻¹). Alike Randles-Sevcik equation, *n*, *A*, *v*, *D* and *c* can be grouped along with 0.620 *F* in *B* (Levich constant) and Eq. [3] can be summarized as Eq. [4].

209
$$I_L = B \,\omega^{1/2}$$
 [4]

210 When plotting I_L vs. $\omega^{1/2}$ (Levich plot) *B* is obtained from the slope of a linear fit and is used to determine 211 the number of electrons transferred *n* or the diffusion coefficient *D*. In our system, we have approximated 212 *v* by 8.90×10^{-3} cm² s⁻¹ corresponding to the kinematic viscosity of 2 M NaClO₄ in water ³⁹. The Tc 213 concentration (0.5 mM) was low enough to neglect its effect on the viscosity.

Combining the slopes of the regression lines from the Randles-Sevcik and the Levich equations, two equations (Eq. [5] and Eq. [6]) are obtained for two unknown variables (D – the diffusion coefficient of Tc in 2 M NaClO₄ and n):

- 217 $Y = 2.69 \times 10^5 A c D^{1/2} n^{3/2}$ [5]
- 218 $B = 0.620 F c A v^{-1/6} D^{2/3} n$ [6]
- 219 Solving this equation system, Eq. [7] and [8] were obtained, directly yielding *D* and *n*, respectively:

$$220 \quad D = \left(\frac{\alpha E}{B}\right)^2 \tag{7}$$

$$221 \qquad n = \frac{\gamma}{\alpha D^{3/2}} \tag{8}$$

222 with $\alpha = 0.620 F c A v^{-1/6}$, $E = (Y/\beta)^{3/2}$ and $\beta = 2.69 \times 10^5 A c$.

223 Since the reduction of Tc(VII) in NaClO₄ appears to follow the same mechanism throughout the pH 224 range 4.0-10.0 according to Figure 1b, we selected pH 2.0 and pH 10.0 for the RDE experiments to 225 encompass the working pH range by measuring the two extremes. The reduction curves of the systems 226 at different angular velocities as well as the cyclic voltammograms at different scan rates are presented 227 in Figures S2 and S3 in the supporting information. Figure 2 shows the Randles-Sevcik and Levich plots of Tc at pH 2.0 and 10.0. There is a clear linear correlation between I_L and $\omega^{1/2}$ as well as for I_p and $u^{1/2}$, 228 229 and, therefore, the values for the slopes B and Y were replaced in Eq. [5] and [6] to obtain D and n at 230 both pH values.

Table 1 summarizes the results of the electrochemical analysis.



Figure 2. (circles) Randles-Sevcik and (squares) Levich plots of 0.5 mM KTcO₄ in 2 M NaClO₄ at different pH
values. a), d) First cathodic peak (CP) at pH 2.0 (-0.318 V). b), e) Second cathodic peak (CP) at pH 2.0 (-0.424
V) c), f) Cathodic peak at pH 10.0 (-0.560 V). Y and B are the Randles-Sevcik and Levich slopes (Eq. [5] and [6]
respectively).

236

Table 1. Reduction mechanism of Tc(VII) in NaClO₄ at pH 2.0 and pH 4.0-10.0 in their respective

CP pH	2.0	4.0-10.0
	$Tc(VII) + 2.3 \pm 0.3 e^{-} \rightarrow Tc(V)$	$Tc(VII) + 3.2 \pm 0.3 e^{-} \rightarrow Tc(IV)$
1	$D = 3.92 \times 10^{-5} \text{cm}^2 \text{s}^{-1}$	$D = 5.75 \times 10^{-6} \text{cm}^2 \text{s}^{-1}$
	$E_{vs RHE} = -0.318 V$	$E_{vs RHE} = -0.560 V$
	$Tc(V) + 1.3 \pm 0.3 e^{-} \rightarrow Tc(IV)$	
2	$D = 2.41 \times 10^{-4} cm^2 s^1$	
	$E_{vs RHE} = -0.424 V$	

238 cathodic peaks (CP) and the associated reduction potential vs reversible hydrogen electrode ($E_{vs RHE}$).

n and *D* were calculated with Equations [7] and [8].

We have found that at pH 2.0 the reduction of Tc(VII) begins with the transfer of 2.3 ± 0.3 electrons yielding Tc(V) as an intermediary oxidation state that subsequently gains further 1.3 ± 0.3 electrons to become Tc(IV). At pH 10.0, the reduction of Tc(VII) is direct with the transfer of 3.2 ± 0.3 electrons to produce Tc(IV). The uncertainties in the number of errors were calculated using the error propagation method described elsewhere ⁴⁰.

245 The electrochemical behavior displayed at pH 2.0 is in good agreement with the Latimer diagram of Tc under acidic conditions ⁴¹ where Tc(VI) is postulated as an intermediary oxidation state during the 246 247 reduction from Tc(VII) to Tc(IV). However, as Tc(VI) is unstable in water, a rapid disproportionation to Tc(VII) and Tc(V) takes place ^{25,27,29}. This supports the electrochemical analysis (Table 1), suggesting 248 249 that the small peak at -0.318 V at pH 2.0 is Tc(V). The potential shift with pH related to Tc(IV) formation 250 (-0.424 V for pH 2 and -0.560 V for pH values 4.0, 6.0, 8.0 and 10.0) can be related to the difference in 251 the pH, as it occurs, for example, with manganese where the reduction from $Mn(VII)O_4^-$ to $Mn(IV)O_2$ 252 has a standard potential of 1.7 V at acidic pH and 0.60 V at alkaline pH, according to Mn Latimer diagrams²⁵. 253

The diffusion coefficients of the electroactive Tc species in NaClO₄ at pH 2.0 were determined as 3.92×10⁻⁵ cm² s⁻¹ for Tc(VII) and 2.41×10⁻⁴ cm² s⁻¹ for Tc(V). At pH 10.0, the diffusion coefficient of Tc(VII) is 5.75×10^{-6} cm² s⁻¹. The starting Tc oxidation state at both pH 2.0 and pH 10.0 is Tc(VII), and, therefore, it is clear that pertechnetate is the electroactive species of the first cathodic peaks (CP) at both pH values. Previous studies on Tc diffusion coefficients in aqueous solution are extremely limited and no value could be found in the presence of a salt that remotely resembles NaClO₄ (like KClO₄ or NaBrO₄). For the sake of comparison the values obtained in our work were contrasted against the diffusion coefficients of Tc in bentonite ⁴², where it was reported that the diffusion coefficient of pertechnetate decreases as pH increases, which is in well agreement with our findings with the RDE for the reduction mechanism of Tc(VII) (Table 1).

264 The oxidation mechanism could not be established because it was not possible to stabilize the reduced Tc aqueous species –theoretically Tc(IV)– at the begin of the experiment. As it will be shown in section 265 266 Solid Analysis, the complete reduction of Tc(VII) led to the formation of a solid deposited on the working 267 electrode (WE), making it impossible to apply the electrochemical analysis presented in this section as it is only feasible for species in solution. It is worth explaining that this issue did not affect the 268 269 determination of the reduction mechanism because both the RDE and the CV experiments were fast 270 enough to avoid the precipitation of the reduced Tc. However, the complete reduction of Tc(VII) 271 necessary to start the RDE experiment for the oxidation takes several hours, giving enough time for the 272 deposition of the reduced Tc solid. However, we can interpret that the second anodic peak (0.798 V at 273 pH 2.0 and around 0.570 V at pH 4.0 – 10.0) in Figure 1b corresponds to the formation of Tc(VII), as 274 this is the highest stable oxidation state in solution for technetium

275

3.2 In-situ spectro-electrochemical analysis of the Tc(VII) reduction

Spectro-electrochemical experiments were performed to follow the electrochemical reduction of Tc(VII)O₄⁻ in NaClO₄ at both pH 2.0 and 10.0. The collected UV-vis spectra are shown in Figure 3. As expected, both spectral data sets display at the beginning of the experiments the characteristic signals of TcO₄⁻ at 247 and 289 nm ²⁴. With the application of the potential staircase, the intensity of these features gradually decreases until both bands finally disappear at the last potential steps, indicating full reduction of Tc(VII). The process was identical at both pH 2.0 and 10.0 (Figure 3 a and b).



Figure 3. UV-vis spectra measured during the electrochemical reduction of 0.5 mM Tc(VII)O₄⁻ in 2 M NaClO₄. a) pH 2.0. b) pH 10.0.

The complete reduction of Tc(VII) yielded a black solid deposited on the WE regardless of the sample pH. Taking into account, that UV-vis spectra confirm the lack of Tc(IV) chloride species with absorption at 234 nm and 338 nm ⁴³, and that Tc(IV) is the final reduction product (Table 1), most likely the formed solid is a Tc(IV)-O species.

The spectroscopic behavior depicted in Figure 3b is in good agreement with the findings of the electrochemical analysis at pH 10.0 with no intermediary oxidation state between Tc(VII) and Tc(IV)during the reduction. Therefore, the occurrence of a Tc signal different from those of Tc(VII) was not expected. However, no spectroscopic evidence of the existence of the Tc(V) species suggested by the electrochemical analysis at pH 2.0 was found. This can be due to an extremely fast transition from Tc(V)to Tc(IV) or simply because the Tc(V) species is not active in the UV-vis range or its absorption coefficient is too low.

296

297 **3.3 Solid analysis**

In order to confirm the chemical identity of the solid obtained after the complete reduction of $Tc(VII)O_4^-$,

Raman spectroscopy, XPS and SEM-EDX were performed. The Raman spectra of the solids at pH 2.0

and 10.0 are shown in Figure 4.



301

Figure 4. Raman spectra of the black solid obtained after the total reduction of 0.5 mM KTcO₄ in 2 M NaClO₄ at
 pH 2.0 and 10.0 in the spectro-electrochemical cell. The Raman spectra of KTcO₄ and NaClO₄ have been added
 for comparison.

306 It can be observed that the Raman spectra are identical for both samples, indicating that the chemical 307 identity of the solids at both pH values is the same, supporting the results in Table 1. The spectra of the 308 samples were compared with the spectra of KTcO₄ and NaClO₄. The bands at 458, 632, 666 and 960 cm⁻¹ 309 were attributed to sodium perchlorate ⁴⁴ recrystallized on the working electrode along with the 310 technetium solid.

The band at 330 cm⁻¹ is assigned to Tc-O vibrations by comparison with the KTcO₄ spectra ^{45,46}. However, it is worth mentioning that according to the literature ^{43,47,48} the Tc-Cl bond presents two bands at 332 and 342 cm⁻¹. While no band around 340 cm⁻¹ is present in the spectra of the samples, the bands appearing at 885 and 913 cm⁻¹ are characteristic of the TcO₄⁻ structure corresponding to Tc-O vibrations ^{45,46}. Therefore, the band at 330 cm⁻¹ is also assigned to the Tc-O vibration and no evidence of Tc-Cl bonding is present in the Raman spectra. This confirms that no interaction between Tc and chlorine species took place during the reduction.

Two bands at 374 and 1107 cm⁻¹ remain unidentified after this assignment. Since the initial components of the samples were KTcO₄, NaClO₄ and water, these two remaining bands can be tentatively assigned to the reduced Tc solid that would be Tc(IV) according to the electroanalysis (Table 1). Previous works 49,50 have reported a signal at 877 cm⁻¹ for TcO₂ that does not appear in the Raman spectra of our samples. There is a possibility that this signal is overlapped by the band at 885 cm⁻¹ but, as no reports for signals at 374 and 1107 cm⁻¹ have been found for TcO₂, we refrain from characterizing the solid samples as technetium dioxide.

In order to confirm the oxidation state of technetium in the solid, XPS and SEM-EDX were applied. The XPS spectra of the solid evaluated in Tc 3d and Cl 2p is presented in Figure 5.

327



Figure 5. XPS spectra of the reduced Tc solid. s) Tc 3d, b) Cl 2p.

329 The Tc 3d spectrum (Figure 5a) shows an intense Tc $3d_{5/2}$ peak at 256.2 eV assigned to Tc(IV) since it is close to the reference value for TcO₂ (256.8 eV ⁵¹). NaClO₄ was present during the recording of the 330 331 XPS spectra of the sample because no further separation or purification of the solid was performed after 332 the reduction of Tc(VII) (see solid analysis in the experimental section). The Cl $2p_{3/2}$ elemental line of NaClO₄ is observed at 208.9 eV binding energy in accordance with its reference at 208.9 eV ⁵². Since 333 334 NaClO₄ degrades under X-ray irradiation and the charge of the sample surface caused by the XPS 335 measurement will change slowly during degradation, charge referencing of elemental lines is not reliable 336 if high degradation of NaClO₄ occurs. This was avoided by using monochromatic Al K_α X-rays, larger analysis area, and short acquisition time. Small portions of chlorite and chloride, i.e. the degradation 337 338 products, are detected at the Cl 2p spectrum (Figure 5b), making the results presented reliable despite the 339 presence of NaClO₄.

Even though XPS cannot be used to establish the structure of the technetium compound, the oxidation state can be unequivocally assigned as Tc(IV). Therefore, the bands found at 374 and 1107 cm⁻¹ in the Raman spectra correspond to Tc(IV). To our knowledge, apart from the band at 877 cm⁻¹ for TcO_2^{43} , no other Raman signals for Tc(IV) have been reported before, making the results of this paper very relevant for the identification of Tc(IV) in other applications, e.g. Tc retention studies by minerals.

The SEM-EDX analysis is presented in Figure S4 in the supporting information. The morphology of the sample depicted in the micrographs shows three regions clearly separated: (1) mainly Na, Cl and O, (2) almost completely Tc and O and (3) indium from the foil on which the sample was prepared. This is consistent with the fact that ClO_4^- had no interaction with Tc and the solid obtained corresponds only to a reduced Tc species bonded to O.

350 4. CONCLUSIONS

The reduction of Tc(VII) in non-complexing media (NaClO₄) has been studied for the first time using spectro-electrochemical methods and electrochemical analysis, combined with other spectroscopic and microscopic techniques.

354 The electrochemical results show that the reaction mechanism depends on the pH. By applying Randles-Sevcik and Levich equations, the number of electrons during electrochemical analysis was determined. 355 356 At pH 2.0, the reduction occurs in two steps with the initial gain of 2.3 ± 0.3 electrons by Tc(VII) to 357 obtain Tc(V), which subsequently receives 1.3 ± 0.3 electrons to form Tc(IV). At pH 4.0-10.0 Tc(VII) is 358 directly reduced to Tc(IV) with the transfer of 3.2 ± 0.3 electrons. The electrochemical reduction of 359 Tc(VII) in NaClO₄ was followed in parallel with UV-vis absorption spectroscopy. Even though no 360 spectroscopic evidence of intermediate Tc(V) could be obtained, UV-vis showed the absence of Tc(IV)chloride species. After the total reduction of Tc(VII) at both pH 2.0 and 10.0, a black solid was formed. 361 362 Raman spectroscopy confirmed that both solids had the same chemical identity despite the initial pH 363 value, whereas SEM-EDX analysis proves that the solid only consists of Tc and O. XPS analysis 364 identified the solids as Tc(IV) and agrees with the obtained CV results and the electrochemical analysis.

In addition to an accurate determination of the electrons transferred in the reduction process depending on the pH, this study has also yielded two Raman signals at 374 and 1107 cm⁻¹ that correspond to the Tc(IV) species formed after the total reduction of Tc(VII). Such Raman features will be relevant to specific questions in environmental engineering for the identification of Tc(IV) compounds that are the products of the reductive immobilization of Tc(VII) by common minerals and could only be identified by the use of more expensive spectroscopies. This work presents fundamental data to understand Tc redox chemistry and its dependence on pH under the simplest aqueous conditions, i.e. in a non-complexing media.

Both results and methodology applied in the electrochemical analysis will serve as valuable references for further studies to identify Tc redox chemistry in complex systems, e.g. in presence of inorganic and organic ligands. These fundamental studies are essential for a realistic and broad picture of the Tc chemical redox and complexation behavior. A basic Tc chemical understanding will also provide a direct impact on environment protection by enhancing Tc remediation strategies in contaminated areas as well as for the safety assessment of nuclear waste repositories.

Furthermore, this work is also the first step towards a future development of spectro-electrochemical techniques. We envision the development of spectro-electrochemistry couplings to characterize the structure of redox-active species at different oxidation states, which will be helpful not only for Tc but also for other redox-active elements whose chemical behavior is still to be fully defined.

383

384 Abbreviations

- 385 CE: counter electrode
- 386 CP: Cathodic peak
- 387 CV: Cyclic voltammetry
- 388 RDE: Rotating disk electrode
- 389 RE: reference electrode
- 390 RHE: Reversible hydrogen electrode
- 391 SEM-EDX: Scanning electron microscopy with energy dispersive X-ray spectroscopy
- 392 WE: working electrode
- 393 XPS: X-ray photoelectron spectroscopy
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Supporting Information. In-house built spectro-electrochemical cell. Reduction curves. CVs at
 different scan rates. SEM-EDX. Experimental description of Tc solid analysis.

397

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