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Features of Ti^{IV} and Sc^{III} behavior in oxalic acid solutions affecting the $^{44}Ti/^{44}Sc$ generating system based on anion exchange resins

Nikolay A. Titchenko, Bayirta V. Egorova and Stepan N. Kalmykov

Calculation of solution composition

All the ratios were calculated for static conditions in equilibrium.

The equilibrium compositions of solutions containing Ti(IV) and separately Sc(III) were calculated for oxalic and hydrochloric acid mixtures, for which the distribution coefficients (K_d) of Ti(IV) and Sc(III) on AG 1X8 resin were obtained by Filosofov et al.[S1]

The calculations were performed using the Hyperquad simulation and speciation (HySS) software[S2]. The stability constants for the complexes $[Ti(OH)_2(Ox)]^0$ and $[Ti(OH)_2(Ox)_2]^{2-}$ were taken from paper[S3]. Data for the other complexes, including scandium complexes, were taken from the HYDRA equilibrium constants database[S4].

When calculating the pH of solutions with given concentrations of oxalic and hydrochloric acid, it was assumed that hydrochloric acid dissociates completely and oxalic acid partially in the first step ($pKa^1 = 1.23$). The total concentration of Ti(IV) in the solutions was $4.2 \cdot 10^{-5}$ M and Sc(III) was $6.38 \cdot 10^{-12}$, giving a concentration of 185 MBq of ^{44}Ti in equilibrium with ^{44}Sc in a 20 mL solution.

The results of the calculations and K_d from paper[S1] are presented in Tables S1–S3 and Figures S7–S9 for Ti(IV), for Sc(III) in Tables S4–S6 and Figures S10–S12.

Materials

The ion exchange resins used in this work were Dowex 1X8 (100-200 mesh, Cl^--form, Sigma-Aldrich), Dowex 1X8 (200-400 mesh, Cl^--form, Sigma-Aldrich), TEVA (Particle size : 100-150 μm, Cl^--form, TrisKem Int.). $^{44}TiCl_4$ solution in 0.1M HCl was ordered from RITVERC. The radioactivity of the samples was measured by gamma spectrometry with HPGe-detector GR3818 Canberra, or HPGe-detector GC3020 Canberra. For scandium - at the 1157 keV or 511 keV line, for titanium - at the 78 keV line. The spectrum was processed using the SpectraLine software (LSRM, Russia). Autoradiography was performed using the Perkin Elmer Cyclone Plus phosphor storage system and the corresponding software.

Methods

Kinetics of sorption of Ti(IV) on resins:

A stock solution of ^{44}Ti in HCl was evaporated and redissolved in 0.005 M H_2Ox. A 500 μL aliquot of the resulting solution was measured on a gamma spectrometer and then added to a sample containing 50 mg of the test resin in a solution of a mixture of hydrochloric and oxalic acids such that the total volume of solution in the resulting sample was 4 mL and the concentration of H_2Ox and HCl corresponded to the test solution. The sample was stirred using a vortex mixer and time counting was started. Immediately after mixing, a first aliquot of 600 μL was taken so that the aliquot contained a suspension of resin particles. The sample was placed on the shaker. Subsequent aliquots were taken after 2.5, 6, 10 and 30 min. Each aliquot was centrifuged immediately after collection to precipitate the resin particles and 500 μL of solution was taken from it and measured on a gamma spectrometer. The activity obtained was compared with the activity of the original aliquot and the fraction of ^{44}Ti remaining in solution at the time of sampling and the fraction of ^{44}Ti sorbed on the resin were calculated.

Determination of static sorption capacity of TEVA

To obtain a solution of stable Ti(IV), a sample of titanium metal chips was dissolved in concentrated hydrochloric acid. A few drops of $HClO_4$ were added to the resulting purple Ti(III) solution to oxidize Ti^{3+} to Ti^{4+}, and the solution became discolored. The Ti(IV) solution was evaporated and redissolved in a known volume of 10 M HCl. The resulting solution with known concentration of Ti(IV) was diluted with oxalic acid and deionized water and used to create the desired concentration of Ti(IV) in the sample, neglecting the concentration of ^{44}Ti. The initial ^{44}Ti was evaporated and redissolved in 0.1 M HCl. To prepare each sample, the required amount of Ti(IV) solution, hydrochloric and oxalic acids were mixed, an aliquot of ^{44}Ti was added and diluted with water to a final solution volume of 40 mL. To the resulting solutions, 50 mg each of TEVA resin was added without prior preparation and

left to shaker. The next day, the samples were centrifuged to precipitate the resin particles and 20 mL each of the solution without resin particles was taken. The resulting solutions were measured on a gamma spectrometer and the amount of Ti(IV) in solution and sorbed by TEVA was calculated. The "reference" sample was not supplemented with stable Ti(IV) solution and resin, the other stages of the experiment were carried out similarly, the calculations of the amount of Ti(IV) sorbed and remaining in solution were carried out relative to this sample. From the data obtained, a saturation curve was plotted (Figure S1) and the static sorption capacity was determined.

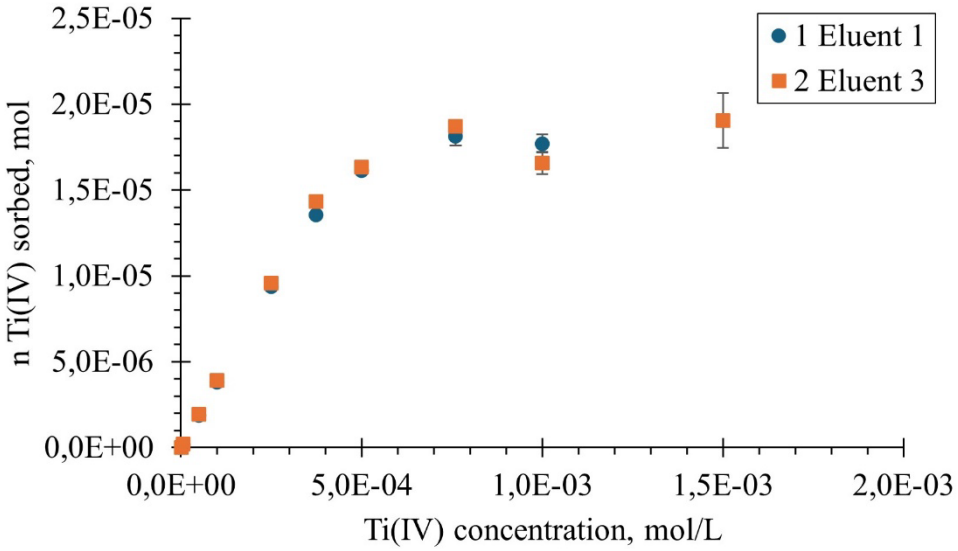

Figure S1 Saturation curve for TEVA and Ti(IV) in media: (1) Eluent 1 (0.005 H_2Ox + 0.065 HCl), (2) Eluent 3 (0.1 H_2Ox + 0.2 HCl).

Determination of distribution coefficients of Ti(IV) and Sc(III) on resins in the eluent 0.005M H_2Ox *+ 0.065M HCl*
To calculate the distribution coefficients (K_d) of Sc(III), the eluate from a TEVA-based generator column obtained by the method described later in the section "Preparation of the laboratory generator column" was used. To calculate the K_d Ti(IV), a solution of ^{44}Ti in HCl was evaporated and ^{44}Ti was redissolved in a solution of 0.005M H_2Ox + 0.065M HCl. Aliquots of the obtained solutions were diluted with 0.005M H_2Ox + 0.065M HCl to a total volume of 650 µL. To the obtained solutions, 0.05 g of the tested resin (except for the "reference" samples) were added without prior preparation. The samples were placed on a shaker for two days for the K_d Ti(IV) study and for 3 hours for the Sc(III) study. The samples were centrifuged to precipitate resin particles, and an aliquot of the resin-free solution was taken and measured on a gamma spectrometer. A decay correction was made for ^{44}Sc. K_d was calculated according to the formula:

$$K_d = \frac{A_0 - A_s}{A_s} \times \frac{V}{m},$$

where: A_0 - specific activity of the aliquot of the solution in the "reference" sample (cps), A_s - specific activity of the aliquot of the solution of the tested sample after sorption (cps), V - volume of the solution (0.65 mL), m - mass of the resin (g).

Preparation and elution of ^{44}Ti/^{44}Sc model generator columns
Pre-soaked resin was placed in a glass column with an inner diameter of 6 mm. In the case of Dowex 1X8 100-200 mesh, the resin volume was 3 mL, 110 mm height; Dowex 1X8 200-400 mesh, 2.4 mL, 85mm height; TEVA, 2.7 mL, 95 mm height. The columns were washed with 10 mL of H2O, and 10 mL of 0.1 M H_2Ox.
The stock solution of ^{44}Ti in HCl was evaporated and redissolved in 3 mL of 0.1 M H_2Ox. The resulting solution was loaded onto a resin column. The activity of ^{44}Ti loaded on the Dowex 1X8 100-200 mesh column was 4.2 kBq; Dowex 1X8 200-400 mesh, 2.5 kBq; and TEVA, 6 kBq.
The column was eluted with a solution of an acidic mixture of 0.065 M HCl + 0.005 M H_2Ox (Eluent 1). The eluent flow through the TEVA and Dowex 1X8 100-200 mesh columns was moved by gravity, and a peristaltic pump was used for Dowex 200-400 mesh. For Dowex 100-200 mesh, the eluent volume was 40-50 mL per elution, elution rate 1 mL/min (flow rate =35mm/min); Dowex 200-400: 20-30 mL, 0.36 mL/min (13 mm/min); and TEVA: 5 mL, 0.4 mL/min (14 mm/min). The ^{44}Sc eluate was collected in 1 mL fractions and each fraction was measured on a gamma spectrometer. The activity values obtained were recalculated with decay correction from

the start of the elution, and elution curves were plotted (Figure S2). Elution was performed no more than once per day.

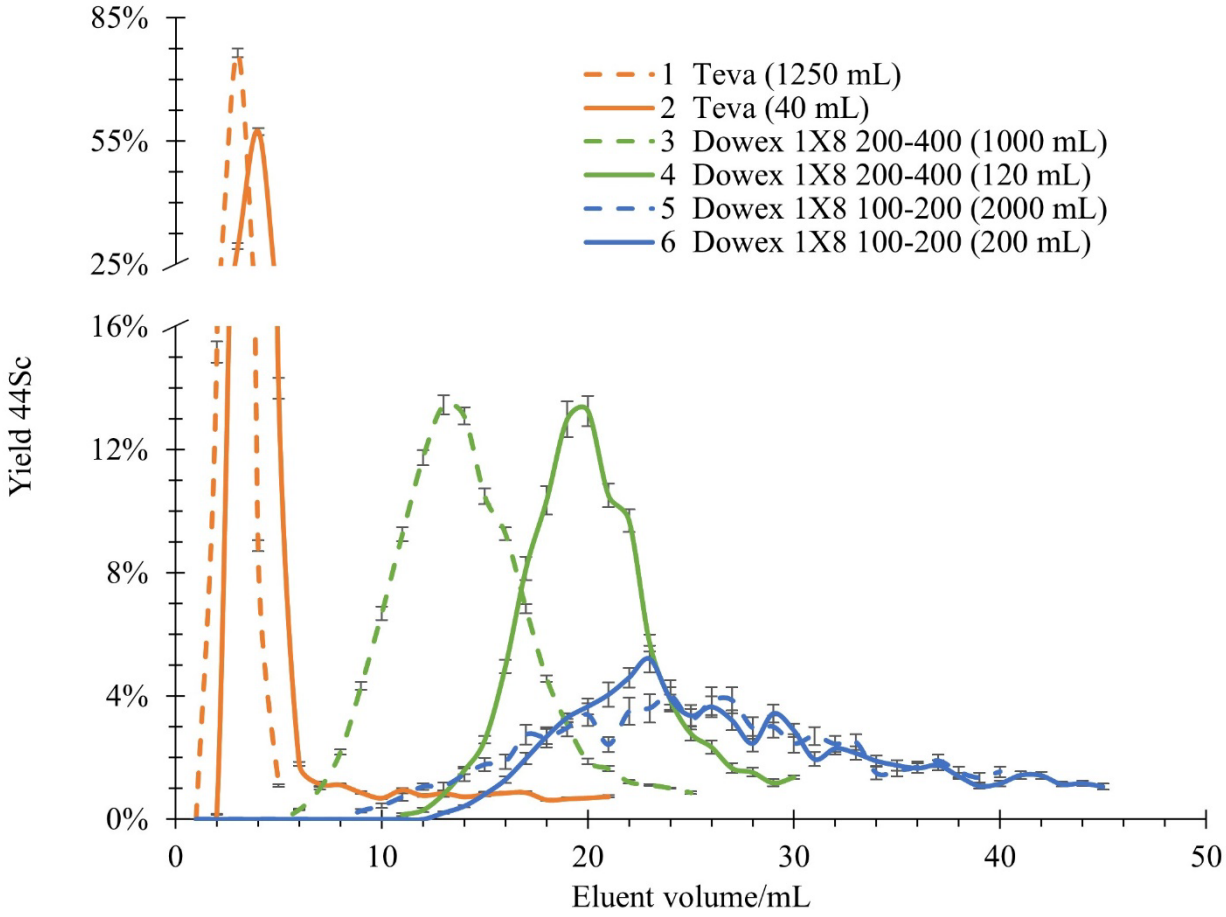

Figure S2 Elution curves of ^{44}Sc from generator columns at the start of operation and after prolonged use: (1) TEVA (1250 mL), (2) TEVA (40 mL), (3) Dowex 1X8 200-400 (1000 mL), (4) Dowex 1X8 200-400 (120 mL), (5) Dowex 1X8 100-200 (2000 mL), (6) Dowex 1X8 100-200 (200 mL). The total volume of eluent passing through the column is given in parentheses. The volume of the fractions is 1 mL.

To simulate long-term use of the Dowex 1X8 and TEVA-based generator systems, elution with Eluent 1 was performed at 200-350 mL per elution for Dowex 1X8 and 100 mL for TEVA. The total eluent volume for Dowex 1X8 100-200 mesh was 1450 mL for 5 elutions and 600 mL for TEVA for 6 elutions. The eluate was collected in 50 mL vials. The eluate from each elution was pooled and evaporated to a volume of 50 mL, incubated for at least 2 days, and measured on a gamma spectrometer to determine the ^{44}Ti breakthrough. After each elution, the distribution of radioactivity in the column was visualized by digital autoradiography. A fixed label was used to control the radioactivity localization zone in the column. The ^{152}Eu label was fixed to the body of each column, which remained stationary relative to the resin throughout the column operation (550 mL of eluent was passed through the column with Dowex 1X8 100-200 mesh, 0 mL with TEVA and Dowex 1X8 100-200 mesh before the label was fixed). The shift of the activity localization zone in the generator columns as used was assessed relative to the ^{152}Eu label by autoradiography (Figures S3 to S5).

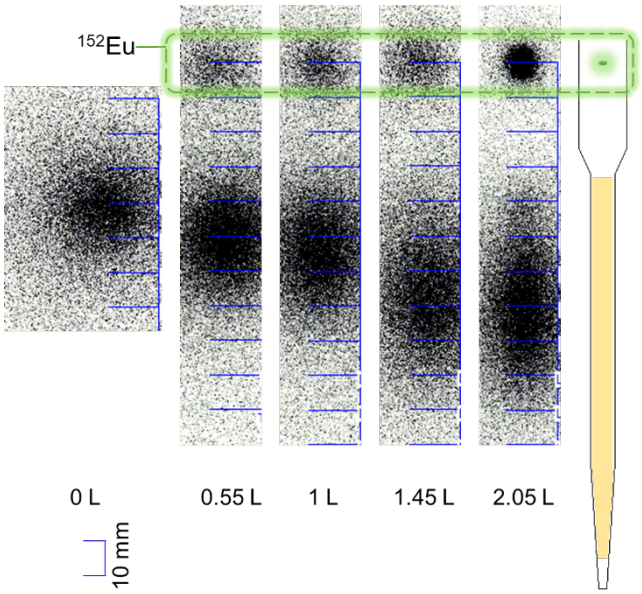

Figure S3 The shift of the radioactivity localization zone in the Dowex 1X8 (100-200 mesh) column relative to the fixed ^{152}Eu. The volume of eluent passed through the column prior to autoradiography is shown below each image. The darkest areas correspond to the zone of maximum activity concentration.

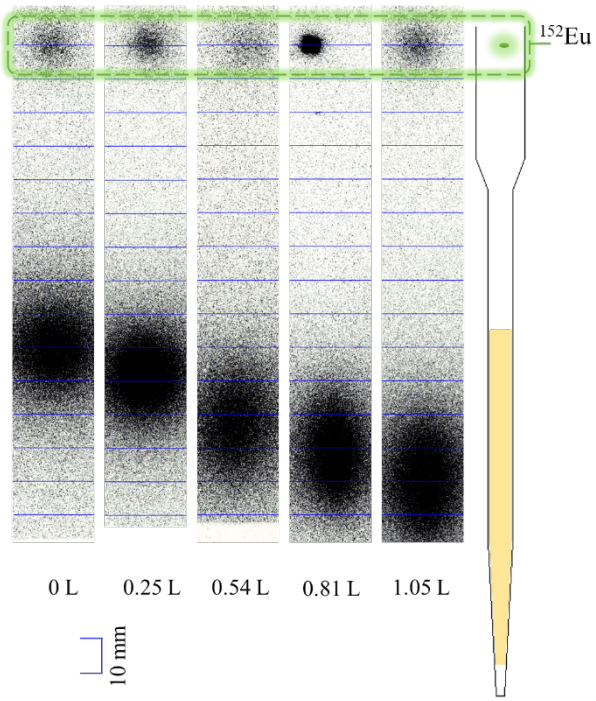

Figure S4 The shift of the radioactivity localization zone in the Dowex 1X8 (200-400 mesh) column relative to the fixed ^{152}Eu. The volume of eluent passed through the column prior to autoradiography is shown below each image. The darkest areas correspond to the zone of maximum activity concentration.

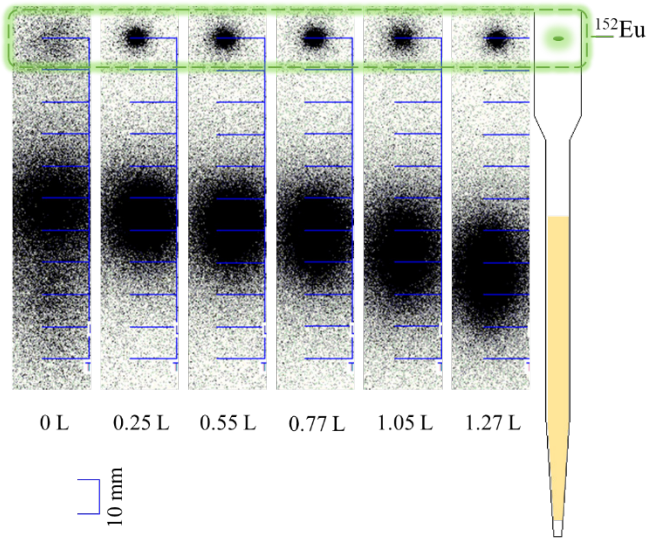

Figure S5 The shift of the radioactivity localization zone in the TEVA column relative to the fixed ^{152}Eu. The volume of eluent passed through the column prior to autoradiography is shown below each image. The darkest areas correspond to the zone of maximum activity concentration.

To roughly estimate the generator lifetime from autoradiographic data, it can be calculated when the center of the ^{44}Ti localization zone moves 80 mm for each model column:

Dowex 1×8 100-200 mesh: The center of the 44Ti spot moves approximately 22 mm in the direction of flow after 1.5 L of eluent (from 550 mL to 2.05 L). One elution requires 50 mL of eluent. This column can be used approximately 110 times (1.5L/22mm×80mm=5.45L, or (5.45/0.05=109)109 elutions).

Dowex 1×8 200-400: The shift of the activity localization center along the column is about 35 mm per 1.05 L of eluent. 1 elution requires 30 mL of solution. This means that this column can be used approximately 80 times (1.05L/35mm×80=2.4L, or (2.4/30)=80 elutions).

Teva: Passing 1.27 L of eluent will shift the center of the 44Ti spot approximately 19 mm. One elution requires 5 mL of solution. The column can be used approximately 1000 times (1.27L/19mm×80mm=5.34L or (5.34/0.005) = 1,068 elutions).

This estimate shows that the TEVA-based generator may allow a significantly higher number of scandium elutions, but this estimate is rather crude and does not take into account the possibility of using the “reverse” elution mode. In addition, this estimate does not account for sorbent degradation due to radiolysis, which will be significant for large amounts of medically relevant activity.

Preparation of the laboratory generator column

The laboratory column with TEVA was prepared similarly to the model columns, the internal dimension of the column was 3.5 mm, resin volume 1 mL, height 100 mm, activity ^{44}Ti 75 kBq, flow rate under gravity 0.26 mL/min (27 mm/min). Elution was performed with Eluent 1, 3 mL each. For ^{44}Sc experiments, the eluate was collected in fractions of 0.5 mL each, and for elution curve construction, in fractions of 0.1±0.02 mL each. Each fraction was measured with a gamma spectrometer. The activity values obtained were recalculated with decay correction from the start of the elution. To measure ^{44}Ti breakthrough, the eluate was remeasured on the gamma spectrometer at least 1 week after elution. The zone of activity localization within the column was determined by autoradiography similar to the model columns (Figure S6).

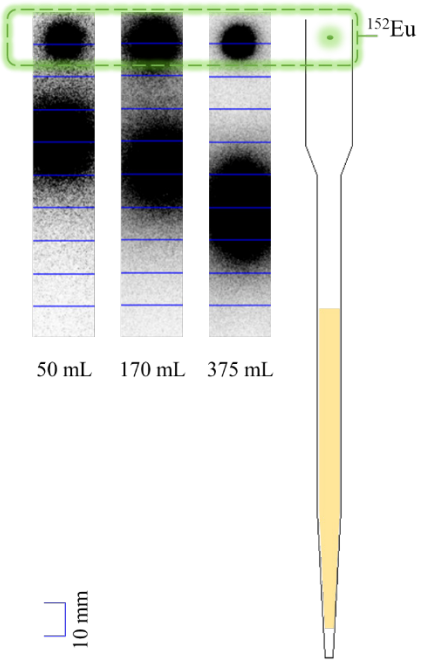

Figure S6 The shift of the radioactivity localization zone in the TEVA based laboratory generator column relative to the fixed ^{152}Eu. The volume of eluent passed through the column prior to autoradiography is shown below each image. The darkest areas correspond to the zone of maximum activity concentration.

Table S1 Calculation results for Ti(IV) in solutions based on 0.1M H_2Ox

Conditions, mol/L								
total Cl	0	0,05	0,1	0,15	**0,2**	0,3	0,5	1
p(H)	1,28	1,05	0,88	0,76	**0,66**	0,5	0,29	0
Results, mol/L								
H-1	3,2E-13	1,9E-13	1,3E-13	9,8E-14	7,8E-14	5,4E-14	3,3E-14	1,7E-14
free Cl	0,0E+00	5,0E-02	1,0E-01	1,5E-01	2,0E-01	3,0E-01	5,0E-01	1,0E+00
ClH	0,0E+00	2,2E-09	6,6E-09	1,3E-08	2,2E-08	4,8E-08	1,3E-07	5,0E-07
free Ox	6,5E-05	2,9E-05	1,5E-05	9,4E-06	6,3E-06	3,2E-06	1,3E-06	3,6E-07
OxH	5,3E-02	4,0E-02	3,1E-02	2,5E-02	2,1E-02	1,6E-02	1,0E-02	5,6E-03
OxH2	4,7E-02	6,0E-02	6,9E-02	7,5E-02	7,9E-02	8,4E-02	9,0E-02	9,4E-02
free Ti(OH)2	5,4E-10	2,5E-09	8,1E-09	1,8E-08	3,6E-08	9,7E-08	3,1E-07	9,4E-07
(Ti(OH)2)H-1	2,0E-10	5,5E-10	1,2E-09	2,1E-09	3,2E-09	6,0E-09	1,2E-08	1,8E-08
(Ti(OH)2)H-2	3,2E-12	5,3E-12	7,8E-12	1,0E-11	1,2E-11	1,6E-11	1,9E-11	1,6E-11
(Ti(OH)2)Cl2	0,0E+00	8,1E-11	1,0E-09	5,3E-09	1,8E-08	1,1E-07	9,9E-07	1,2E-05
(Ti(OH)2)Ox	2,8E-06	5,8E-06	9,8E-06	1,4E-05	1,8E-05	2,5E-05	3,2E-05	2,7E-05
(Ti(OH)2)Ox2	3,9E-05	3,6E-05	3,2E-05	2,8E-05	2,4E-05	1,7E-05	9,0E-06	2,1E-06
Ti(OH)2H-2(s)	0,0E+00	0,0E+00	0,0E+00	0,0E+00	0,0E+00	0,0E+00	0,0E+00	0,0E+00
Sum of species (Figure S7)								
Anionic Ti(IV)	93,42%	86,29%	76,76%	67,23%	57,70%	40,99%	21,40%	5,01%
Neutral Ti(IV)	6,57%	13,70%	23,22%	32,72%	42,21%	58,76%	77,84%	92,70%
Cationic Ti(IV)	0,00%	0,01%	0,02%	0,05%	0,09%	0,24%	0,76%	2,28%
K_d^{S1}	>1000	>1000	>1000	>1000	>1000	370	105	17

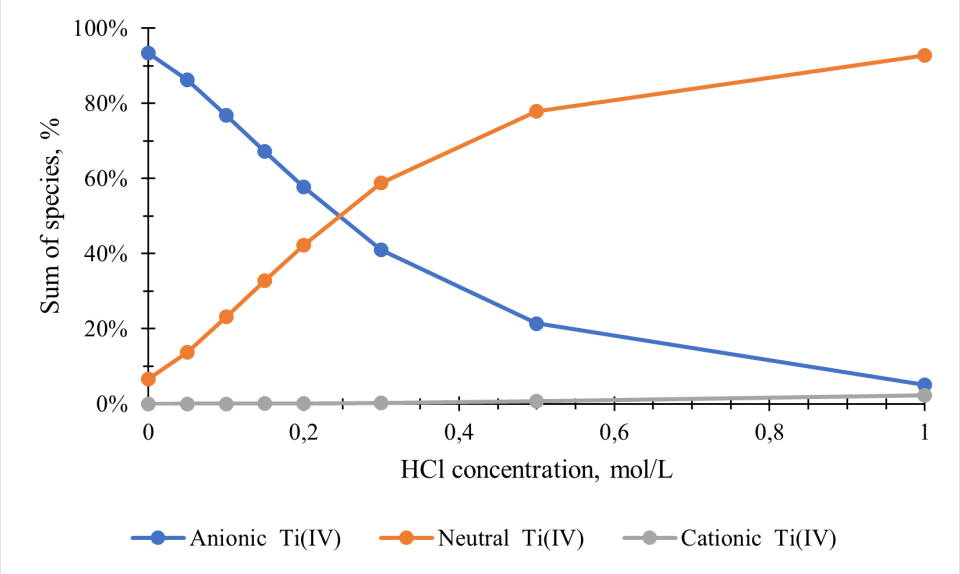

Figure S7 Calculated molar fractions of cationic, anionic and neutral species of Ti^{IV} in solutions based on 0.1M H_2Ox.

Table S2 Calculation results for Ti(IV) in solutions based on 0.025M H_2Ox

Conditions, mol/L							
total Cl	0	0,025	0,05	0,075	**0,125**	0,175	0,25
p(H)	1,72	1,4	1,21	1,07	**0,88**	0,74	0,59
Results, mol/L							
H-1	8,9E-13	4,3E-13	2,8E-13	2,0E-13	1,3E-13	9,3E-14	6,6E-14
free Cl	0,0E+00	2,5E-02	5,0E-02	7,5E-02	1,3E-01	1,8E-01	2,5E-01
ClH	0,0E+00	5,0E-10	1,5E-09	3,2E-09	8,3E-09	1,6E-08	3,2E-08
free Ox	6,4E-05	2,4E-05	1,3E-05	7,7E-06	3,8E-06	2,2E-06	1,2E-06
OxH	1,9E-02	1,5E-02	1,2E-02	1,0E-02	7,7E-03	6,1E-03	4,7E-03
OxH2	6,1E-03	1,0E-02	1,3E-02	1,5E-02	1,7E-02	1,9E-02	2,0E-02
free Ti(OH)2	5,6E-10	3,5E-09	1,1E-08	2,5E-08	7,7E-08	1,6E-07	3,5E-07
(Ti(OH)2)H-1	5,7E-10	1,7E-09	3,5E-09	5,8E-09	1,1E-08	1,8E-08	2,7E-08
(Ti(OH)2)H-2	2,5E-11	3,7E-11	4,8E-11	5,8E-11	7,3E-11	8,3E-11	8,9E-11
(Ti(OH)2)Cl2	0,0E+00	2,8E-11	3,5E-10	1,8E-09	1,5E-08	6,5E-08	2,9E-07
(Ti(OH)2)Ox	2,8E-06	6,7E-06	1,1E-05	1,6E-05	2,3E-05	2,8E-05	3,3E-05
(Ti(OH)2)Ox2	3,9E-05	3,5E-05	3,1E-05	2,6E-05	1,9E-05	1,3E-05	8,4E-06
Ti(OH)2H-2(s)	0,0E+00	0,0E+00	0,0E+00	0,0E+00	0,0E+00	0,0E+00	0,0E+00
Sum of species (Figure S8)							
Anionic Ti(IV)	93,30%	84,04%	73,58%	62,80%	45,09%	31,94%	20,03%
Neutral Ti(IV)	6,70%	15,94%	26,39%	37,13%	54,70%	67,63%	79,06%
Cationic Ti(IV)	0,00%	0,01%	0,03%	0,07%	0,21%	0,43%	0,91%
K_d^{S1}	>1000	>1000	>1000	>1000	1050	410	290

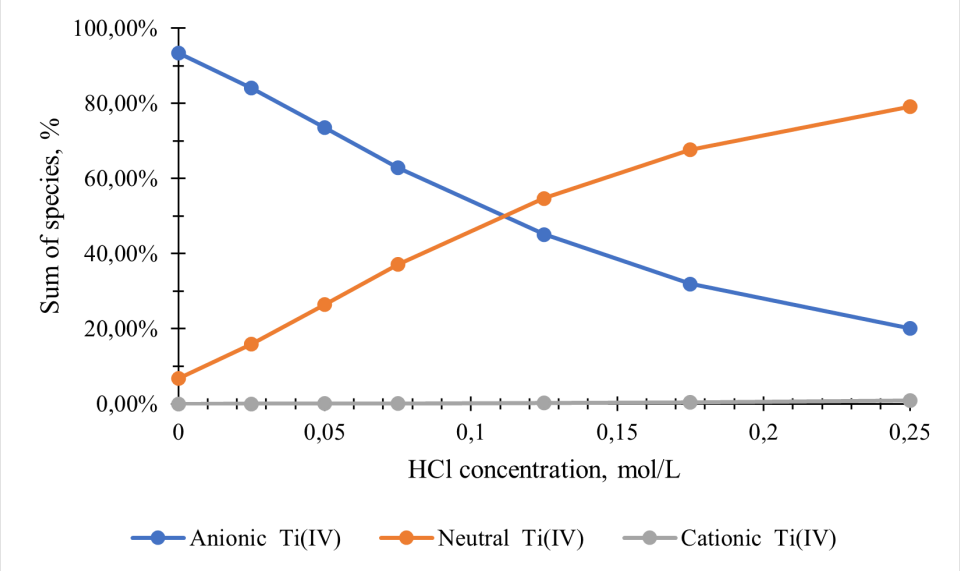

Figure S8 Calculated molar fractions of cationic, anionic and neutral species of Ti^{IV} in solutions based on 0.025M H_2Ox.

Table S3 Calculation results for Ti(IV) in solutions based on 0.005M H_2Ox

Conditions, mol/L										
total Cl	0	0,025	0,0375	0,05	**0,065**	0,08	0,1	0,125	0,25	0,5
p(H)	2,33	1,6	1,43	1,3	**1,19**	1,1	1	0,9	0,6	0,3
Results, mol/L										
H-1	3,6E-12	6,8E-13	4,6E-13	3,4E-13	2,6E-13	2,1E-13	1,7E-13	1,3E-13	6,8E-14	3,4E-14
free Cl	0,0E+00	2,5E-02	3,8E-02	5,0E-02	6,5E-02	8,0E-02	1,0E-01	1,3E-01	2,5E-01	5,0E-01
ClH	0,0E+00	3,1E-10	7,0E-10	1,3E-09	2,1E-09	3,2E-09	5,0E-09	7,9E-09	3,1E-08	1,3E-07
free Ox	6,2E-05	8,9E-06	5,3E-06	3,4E-06	2,4E-06	1,7E-06	1,2E-06	8,1E-07	2,4E-07	6,7E-08
OxH	4,5E-03	3,4E-03	3,0E-03	2,7E-03	2,4E-03	2,1E-03	1,8E-03	1,6E-03	9,4E-04	5,2E-04
OxH2	3,6E-04	1,5E-03	1,9E-03	2,3E-03	2,6E-03	2,8E-03	3,1E-03	3,4E-03	4,0E-03	4,5E-03
free Ti(OH)2	5,8E-10	2,0E-08	4,7E-08	8,8E-08	1,5E-07	2,2E-07	3,5E-07	5,5E-07	1,9E-06	4,3E-06
(Ti(OH)2)H-1	2,4E-09	1,6E-08	2,5E-08	3,4E-08	4,4E-08	5,5E-08	6,8E-08	8,4E-08	1,5E-07	1,7E-07
(Ti(OH)2)H-2	4,4E-10	5,3E-10	5,6E-10	5,8E-10	5,9E-10	5,9E-10	5,8E-10	5,7E-10	5,0E-10	2,9E-10
(Ti(OH)2)Cl2	0,0E+00	1,6E-10	8,5E-10	2,8E-09	8,0E-09	1,8E-08	4,5E-08	1,1E-07	1,5E-06	1,4E-05
(Ti(OH)2)Ox	2,9E-06	1,4E-05	2,0E-05	2,4E-05	2,8E-05	3,0E-05	3,3E-05	3,5E-05	3,6E-05	2,3E-05
(Ti(OH)2)Ox2	3,9E-05	2,8E-05	2,2E-05	1,8E-05	1,4E-05	1,1E-05	8,5E-06	6,2E-06	1,9E-06	3,4E-07
Ti(OH)2H-2(s)	0,0E+00	0,0E+00	0,0E+00	0,0E+00	0,0E+00	0,0E+00	0,0E+00	0,0E+00	0,0E+00	0,0E+00
Sum of species (Figure S9)										
Anionic Ti(IV)	93,14%	65,93%	53,38%	42,78%	33,86%	27,05%	20,35%	14,78%	4,60%	0,81%
Neutral Ti(IV)	6,85%	33,98%	46,45%	56,93%	65,68%	72,29%	78,65%	83,72%	90,53%	88,47%
Cationic Ti(IV)	0,01%	0,09%	0,17%	0,29%	0,46%	0,66%	1,00%	1,50%	4,87%	10,72%
K_d^{S1}	>1000	>1000	>1000	>1000	>1000	844	688	457	46	3,8

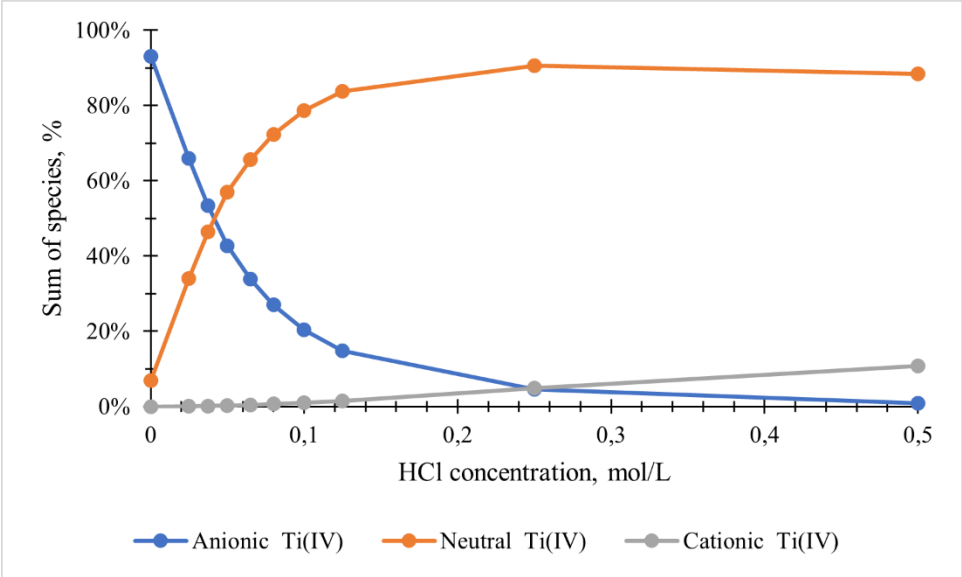

Figure S9 Calculated molar fractions of cationic, anionic and neutral species of Ti^{IV} in solutions based on 0.005M H_2Ox

Table S4 Calculation results for Sc(III) in solutions based on 0.1M H_2Ox

Conditions, mol/L								
total Cl	0	0,05	0,1	0,15	**0,2**	0,3	0,5	1
p(H)	1,28	1,05	0,88	0,76	**0,66**	0,5	0,29	0
Results, mol/L								
H-1	3,2E-13	1,9E-13	1,3E-13	9,8E-14	7,8E-14	5,4E-14	3,3E-14	1,7E-14
free Cl	0,0E+00	5,0E-02	1,0E-01	1,5E-01	2,0E-01	3,0E-01	5,0E-01	1,0E-01
ClH	0,0E+00	2,2E-09	6,6E-09	1,3E-08	2,2E-08	4,8E-08	1,3E-07	5,0E-07
free Ox	6,5E-05	2,9E-05	1,5E-05	9,4E-06	6,3E-06	3,2E-06	1,3E-06	3,6E-07
OxH	5,3E-02	4,0E-02	3,1E-02	2,5E-02	2,1E-02	1,6E-02	1,0E-02	5,6E-03
OxH2	4,7E-02	6,0E-02	6,9E-02	7,5E-02	7,9E-02	8,4E-02	9,0E-02	9,4E-02
free Sc	4,1E-17	5,8E-17	7,6E-17	9,4E-17	1,1E-16	1,5E-16	2,4E-16	4,4E-16
ScH-1	3,9E-20	3,3E-20	2,9E-20	2,7E-20	2,6E-20	2,5E-20	2,3E-20	2,2E-20
ScH-2	3,0E-24	1,5E-24	8,8E-25	6,2E-25	4,7E-25	3,1E-25	1,8E-25	8,8E-26
ScH-3	2,2E-29	6,5E-30	2,7E-30	1,4E-30	8,6E-31	3,9E-31	1,4E-31	3,5E-32
ScH-4	5,4E-38	9,2E-39	2,5E-39	1,0E-39	5,0E-40	1,5E-40	3,4E-41	4,4E-42
Sc2H-2	6,0E-37	4,2E-37	3,4E-37	3,0E-37	2,7E-37	2,4E-37	2,1E-37	2,0E-37
Sc3H-5	7,8E-60	1,6E-60	5,1E-61	2,4E-61	1,3E-61	5,4E-62	1,7E-62	4,0E-63
ScOx	3,2E-11	2,0E-11	1,4E-11	1,1E-11	8,5E-12	6,0E-12	3,7E-12	1,9E-12
ScOx2	9,3E-12	2,6E-12	9,4E-13	4,5E-13	2,4E-13	8,5E-14	2,1E-14	3,1E-15
ScOx3	1,5E-13	1,9E-14	3,6E-15	1,1E-15	3,8E-16	7,0E-17	7,1E-18	2,8E-19
ScOx4	3,7E-17	2,0E-18	2,0E-19	3,7E-20	8,7E-21	8,2E-22	3,4E-23	3,7E-25
ScOxH	2,8E-10	3,0E-10	3,0E-10	3,1E-10	3,1E-10	3,1E-10	3,2E-10	3,2E-10
ScH-3(s)	0,0E+00	0,0E+00	0,0E+00	0,0E+00	0,0E+00	0,0E+00	0,0E+00	0,0E+00
Sum of species (Figure S10)								
Anionic Sc(III)	2,95%	0,81%	0,30%	0,14%	0,07%	0,03%	0,01%	0,00%
Neutral Sc(III)	0,00%	0,00%	0,00%	0,00%	0,00%	0,00%	0,00%	0,00%
Cationic Sc(III)	97,05%	99,19%	99,70%	99,86%	99,93%	99,97%	99,99%	100,00%
K_d^{S1}	184	41	14	5,1	1,7	0,2	0	0

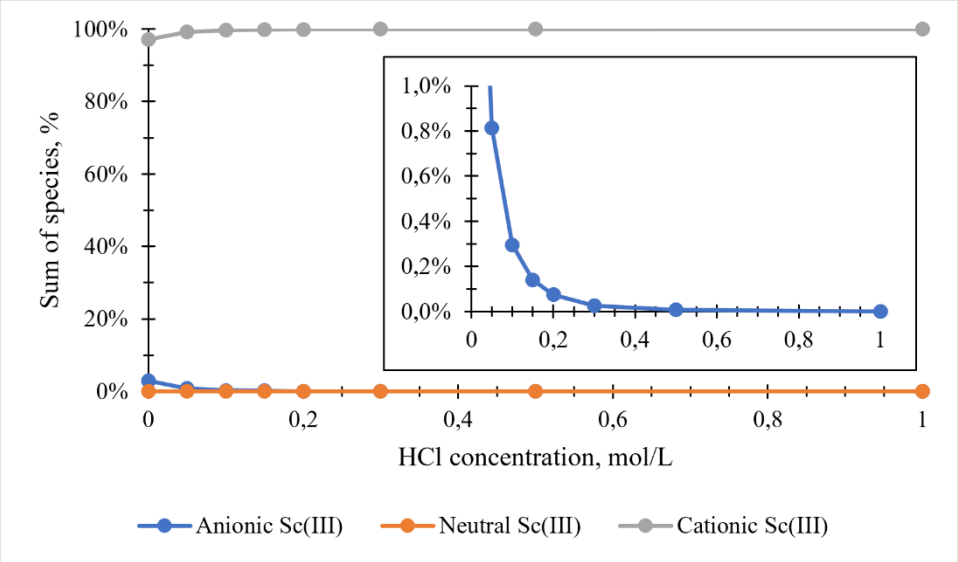

Figure S10 Calculated molar fractions of cationic, anionic and neutral species of Sc^{III} in solutions based on 0.1M H_2Ox.

Table S5 Calculation results for Sc(III) in solutions based on 0.025M H_2Ox

Conditions, mol/L							
total Cl	0	0,025	0,05	0,075	**0,125**	0,175	0,25
p(H)	1,72	1,4	1,21	1,07	**0,88**	0,74	0,59
Results, mol/L							
H-1	8,9E-13	4,3E-13	2,8E-13	2,0E-13	1,3E-13	9,3E-14	6,6E-14
free Cl	0,0E+00	2,5E-02	5,0E-02	7,5E-02	1,3E-01	1,8E-01	2,5E-01
ClH	0,0E+00	5,0E-10	1,5E-09	3,2E-09	8,3E-09	1,6E-08	3,2E-08
free Ox	6,4E-05	2,4E-05	1,3E-05	7,8E-06	3,8E-06	2,2E-06	1,2E-06
OxH	1,9E-02	1,5E-02	1,2E-02	1,0E-02	7,7E-03	6,1E-03	4,7E-03
OxH2	6,1E-03	1,0E-02	1,3E-02	1,5E-02	1,7E-02	1,9E-02	2,0E-02
free Sc	9,3E-17	1,4E-16	1,8E-16	2,3E-16	3,1E-16	3,9E-16	5,2E-16
ScH-1	2,5E-19	1,8E-19	1,5E-19	1,3E-19	1,2E-19	1,1E-19	1,0E-19
ScH-2	5,1E-23	1,8E-23	9,6E-24	6,2E-24	3,5E-24	2,4E-24	1,6E-24
ScH-3	1,1E-27	1,8E-28	6,2E-29	2,9E-29	1,1E-29	5,2E-30	2,4E-30
ScH-4	7,1E-36	5,7E-37	1,3E-37	4,3E-38	1,0E-38	3,6E-39	1,2E-39
Sc2H-2	2,4E-35	1,3E-35	8,9E-36	7,0E-36	5,4E-36	4,6E-36	4,1E-36
Sc3H-5	1,5E-56	1,3E-57	3,2E-58	1,2E-58	3,3E-59	1,4E-59	5,7E-60
ScOx	7,2E-11	4,1E-11	2,8E-11	2,1E-11	1,4E-11	1,0E-11	7,3E-12
ScOx2	2,0E-11	4,5E-12	1,6E-12	7,3E-13	2,4E-13	9,9E-14	3,8E-14
ScOx3	3,4E-13	2,8E-14	5,3E-15	1,5E-15	2,3E-16	5,5E-17	1,1E-17
ScOx4	7,8E-17	2,4E-18	2,5E-19	4,1E-20	3,1E-21	4,3E-22	4,9E-23
ScOxH	2,3E-10	2,7E-10	2,9E-10	3,0E-10	3,0E-10	3,1E-10	3,1E-10
ScH-3(s)	0,0E+00	0,0E+00	0,0E+00	0,0E+00	0,0E+00	0,0E+00	0,0E+00
Sum of species (Figure S11)							
Anionic Sc(III)	6,51%	1,41%	0,51%	0,23%	0,07%	0,03%	0,01%
Neutral Sc(III)	0,00%	0,00%	0,00%	0,00%	0,00%	0,00%	0,00%
Cationic Sc(III)	93,49%	98,59%	99,49%	99,77%	99,93%	99,97%	99,99%
K_d^{S1}	954	168	40,9	14,2	2,68	0,3	0

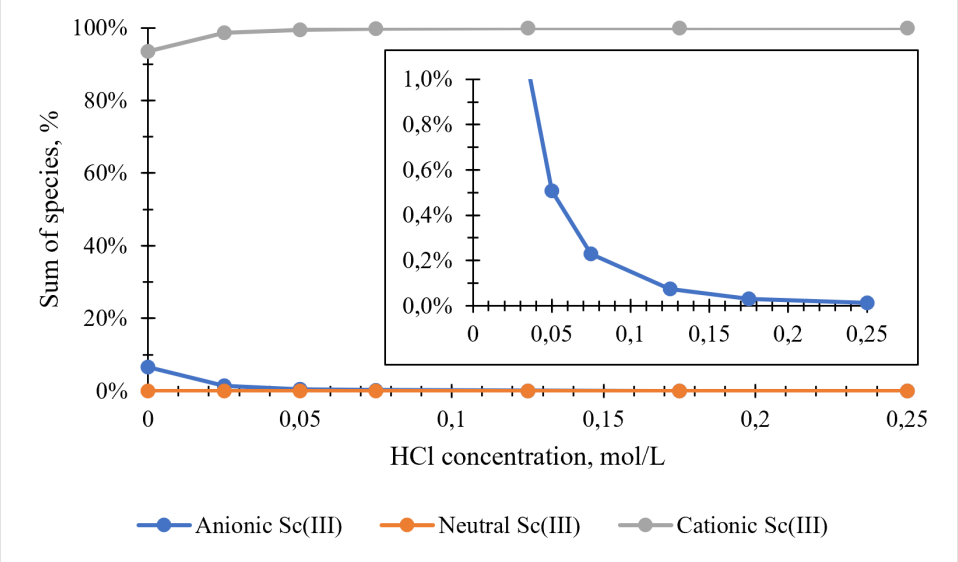

Figure S11 Calculated molar fractions of cationic, anionic and neutral species of Sc^{III} in solutions based on 0.025M H_2Ox.

Table S6 Calculation results for Sc(III) in solutions based on 0.005M H_2Ox

Conditions, mol/L										
total Cl	0	0,025	0,0375	0,05	**0,065**	0,08	0,1	0,125	0,25	0,5
p(H)	2,33	1,6	1,43	1,3	**1,19**	1,1	1	0,9	0,6	0,3
Results, mol/L										
H-1	3,6E-12	6,8E-13	4,6E-13	3,4E-13	2,6E-13	2,1E-13	1,7E-13	1,3E-13	6,8E-14	3,4E-14
free Cl	0,0E+00	2,5E-02	3,8E-02	5,0E-02	6,5E-02	8,0E-02	1,0E-01	0,125	0,25	0,5
ClH	0,0E+00	3,1E-10	7,0E-10	1,3E-09	2,1E-09	3,2E-09	5,0E-09	7,9E-09	3,1E-08	1,3E-07
free Ox	6,3E-05	9,0E-06	5,3E-06	3,5E-06	2,4E-06	1,7E-06	1,2E-06	8,2E-07	2,4E-07	6,8E-08
OxH	4,6E-03	3,5E-03	3,1E-03	2,7E-03	2,4E-03	2,1E-03	1,9E-03	1,6E-03	9,5E-04	5,3E-04
OxH2	3,6E-04	1,5E-03	1,9E-03	2,3E-03	2,6E-03	2,9E-03	3,1E-03	3,4E-03	4,1E-03	4,5E-03
free Sc	2,0E-16	5,7E-16	6,9E-16	8,2E-16	9,5E-16	1,1E-15	1,3E-15	1,5E-15	2,5E-15	4,7E-15
ScH-1	2,2E-18	1,1E-18	9,4E-19	8,2E-19	7,4E-19	6,8E-19	6,3E-19	5,9E-19	5,1E-19	4,7E-19
ScH-2	1,9E-21	1,8E-22	1,0E-22	6,5E-23	4,5E-23	3,4E-23	2,5E-23	1,9E-23	8,1E-24	3,7E-24
ScH-3	1,6E-25	2,8E-27	1,1E-27	5,2E-28	2,8E-28	1,7E-28	1,0E-28	5,9E-29	1,3E-29	2,9E-30
ScH-4	4,3E-33	1,4E-35	3,6E-36	1,3E-36	5,5E-37	2,7E-37	1,3E-37	5,9E-38	6,4E-39	7,4E-40
Sc2H-2	1,9E-33	5,1E-34	3,5E-34	2,7E-34	2,2E-34	1,9E-34	1,6E-34	1,4E-34	1,0E-34	8,6E-35
Sc3H-5	1,7E-52	8,3E-55	2,2E-55	7,9E-56	3,5E-56	1,8E-56	9,1E-57	4,7E-57	7,6E-58	1,5E-58
ScOx	1,5E-10	6,1E-11	4,4E-11	3,4E-11	2,7E-11	2,2E-11	1,8E-11	1,5E-11	7,5E-12	3,8E-12
ScOx2	4,4E-11	2,5E-12	1,1E-12	5,3E-13	2,9E-13	1,7E-13	9,7E-14	5,3E-14	8,1E-15	1,1E-15
ScOx3	7,1E-13	5,7E-15	1,4E-15	4,7E-16	1,8E-16	7,7E-17	3,0E-17	1,1E-17	5,1E-19	2,0E-20
ScOx4	1,6E-16	1,9E-19	2,8E-20	6,0E-21	1,5E-21	4,8E-22	1,3E-22	3,3E-23	4,5E-25	4,9E-27
ScOxH	1,2E-10	2,6E-10	2,7E-10	2,8E-10	2,9E-10	3,0E-10	3,0E-10	3,0E-10	3,1E-10	3,2E-10
ScH-3(s)	0,0E+00	0,0E+00	0,0E+00	0,0E+00	0,0E+00	0,0E+00	0,0E+00	0	0	0
Sum of species (Figure S12)										
Anionic Sc(III)	13,89%	0,77%	0,33%	0,17%	0,09%	0,05%	0,03%	0,02%	0,00%	0,00%
Neutral Sc(III)	0,00%	0,00%	0,00%	0,00%	0,00%	0,00%	0,00%	0,00%	0,00%	0,00%
Cationic Sc(III)	86,11%	99,23%	99,67%	99,83%	99,91%	99,95%	99,97%	99,98%	100,00%	100,00%
K_d^{S1}	2340	67,2	24	10,9	4	1,27	0,71	0	0	0

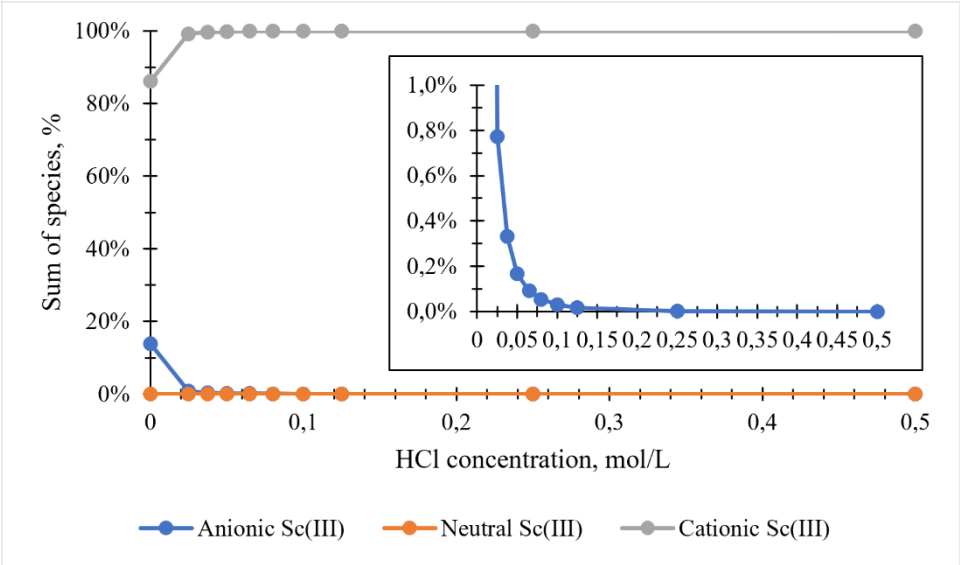

Figure S12 Calculated molar fractions of cationic, anionic and neutral species of Sc^{III} in solutions based on 0.005M H_2Ox.

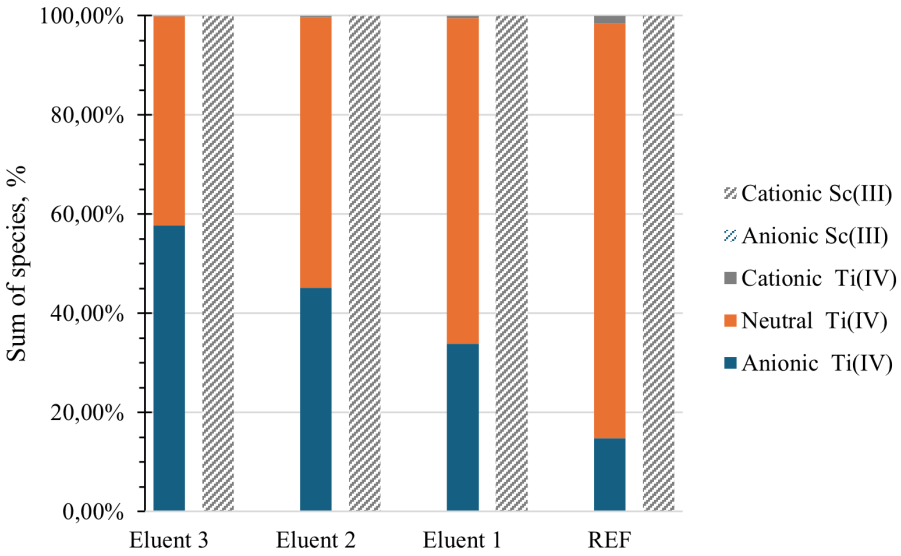

Figure S13 Calculated molar fractions of cationic, anionic and neutral species of Sc^{III} and Ti^{IV} in solutions for kinetics of sorption of Ti^{IV} experiment.

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