Electronic Supplementary Information (ESI)

First Evidence for the Formation of Tc Oxosulfide Complexes: Synthesis, Structure and Characterization

Maryline Ferrier, Philippe F. Weck, Frederic Poineau, Eunja Kim, Alan Stebbins, Longzhou Ma, Alfred P. Sattelberger and Kenneth R. Czerwinski

Rhenium. To better ascertain the validity and reliability of the procedure used in this study, a synthesis of ReO_3S^- was performed following the method described by Partyka and Holm[1] and the UV-Visible and electrospray analyses were performed on the products formed.
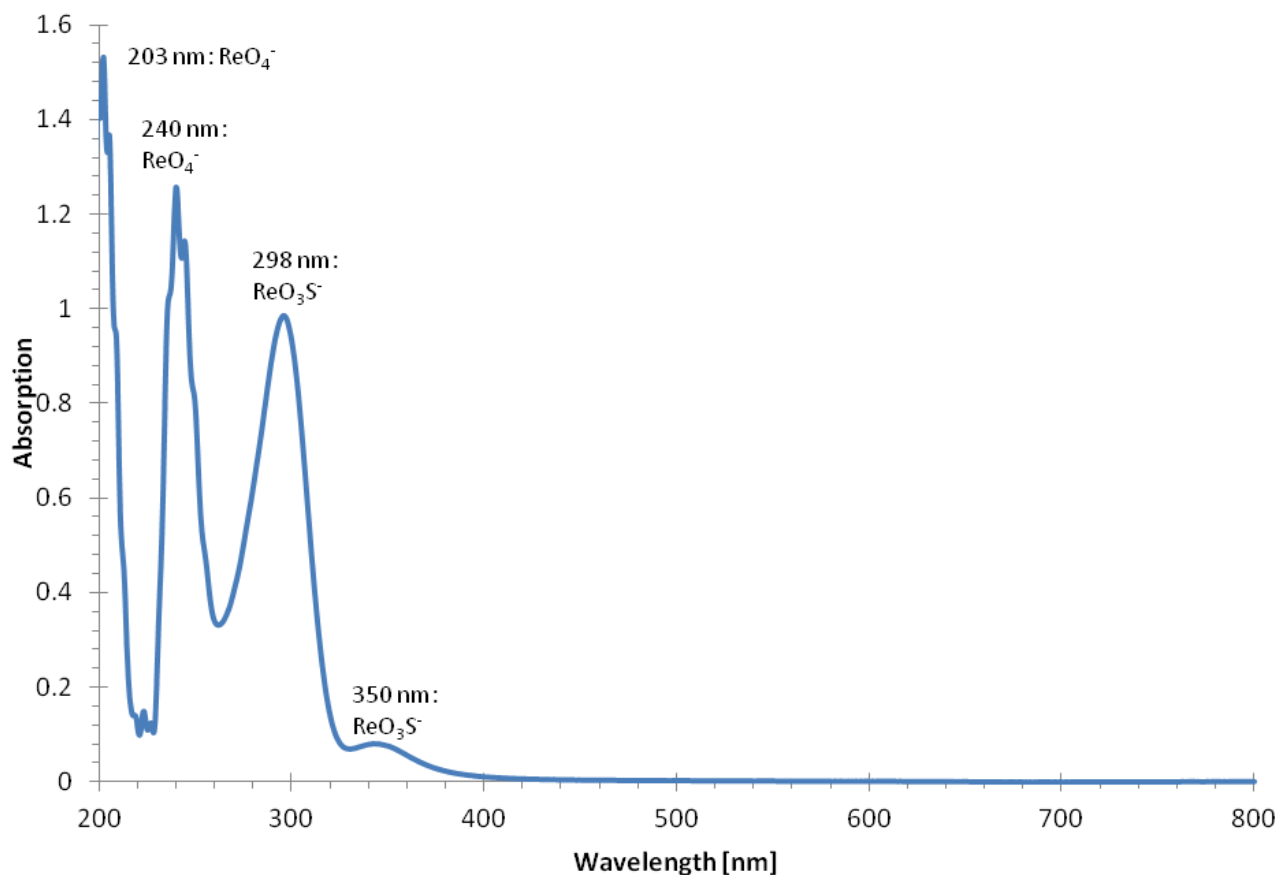

Figure S1. UV-Visible spectrum of tetrabutylammonium perrhenate reacting with bis(trimethylsilyl) sulfide in acetonitrile.

When we compare our results with previous data (cf. Table S1), we see that the solid retrieved at the end of the reaction is a mixture of perrhenate reagent and ReO_3S^-. According to the literature,[2] ReO_3S^- should be yellow with absorption peaks in the UV-Visible range at 350, 298 and 215 nm. The molecular masses expected are 250 for the perrhenate ion and 266 for ReO_3S^-.

Table S1. Comparison of UV-Vis peaks for various Re-containing species

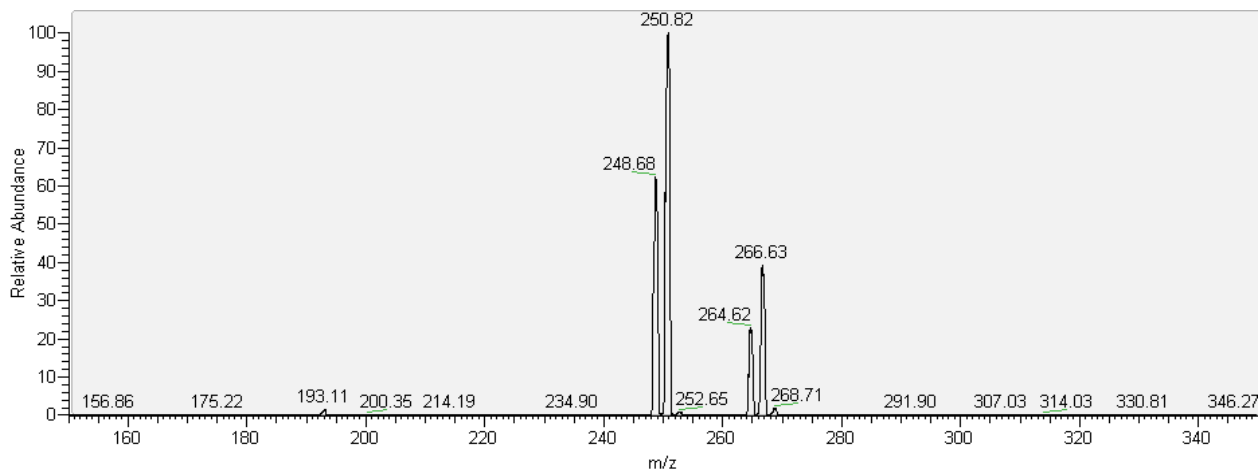| Compounds	Color	UV-Vis peaks [cm^{-1}]	Uv-Vis peaks [nm]
ReO_4^-	White	49, 42 (Ref. 3)	204, 238
ReO_3S^-	Yellow	28.6, 33.6, 46.5 (Ref. 4)	350, 298, 215
$ReO_2S_2^-$	Orange	25, 32 (Ref. 4)	400, 312.5
$ReOS_3^-$	Red	19.8, 25.5, 32.3 (Ref. 4)	505, 392, 309.5
ReS_4^-	Purple	19.8, 28.7, 32.0, 44.0 (Ref. 4)	505, 348, 312, 227

Figure S2. ESI/MS spectrum of tetrabutylammonium perrhenate reacting with bis(trimethylsilyl) sulfide in acetonitrile.

The two peaks observed correspond to ReO_4^- and ReO_3S^-. The spectrum shows different peaks around m/z = 250 and 266 due to the isotopic abundance of rhenium, i.e. for Re-185, M = 184.952977 (37.40 %), and for Re-187, M = 186.955765 (62.60 %).[5]

Long kinetics UV-Visible results

In order to observe the growth of the peak at 360 nm (in Figure S3) and know exactly when the compound started to decompose, the height of each peak was measured. The height corresponded to the difference between the absorption value of the peak at 360 nm and the absorption value of the point corresponding to the intersection of the peak's slope at 360 nm (Cf. Table S2).
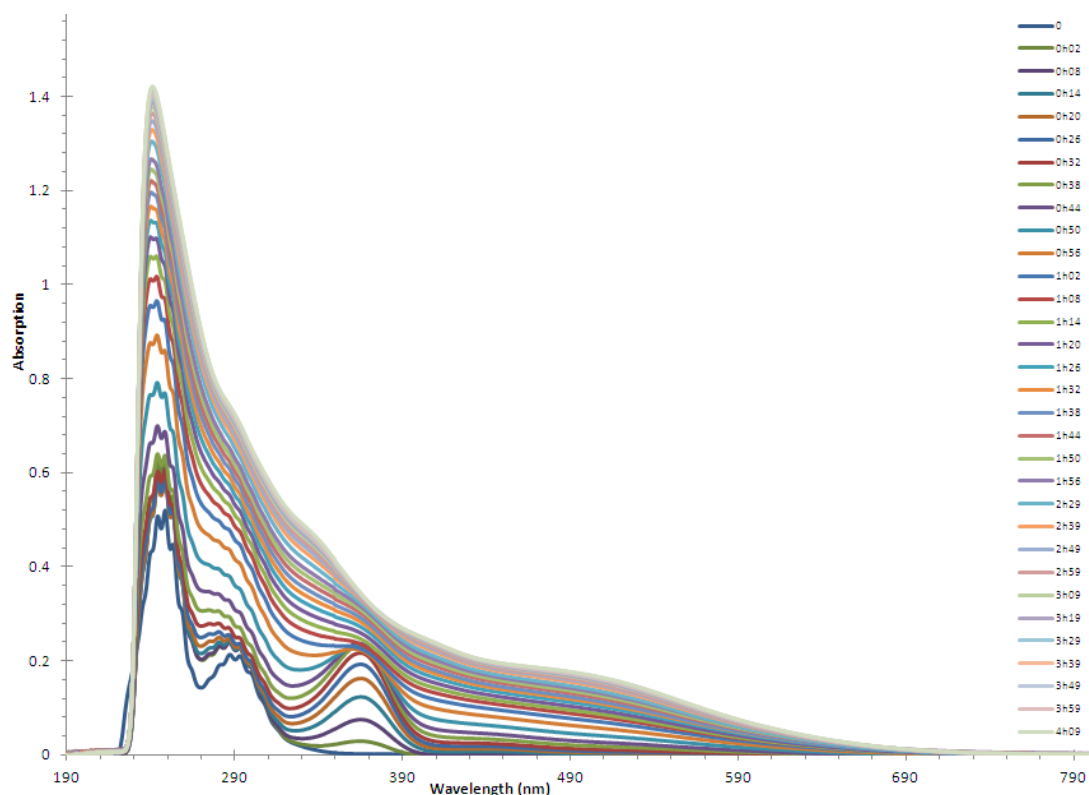
Figure S3. Time evolution of the experimental UV-Visible spectrum of tetrabutylammonium pertechnetate reacting with bis(trimethylsilyl) sulfide with an acetonitrile baseline correction.

Table S2. Value used to determine the height of the peak at 360 nm over time.

| Time	Absorption value at 360 nm	Absorption value of the intersection	Height of the peak
0h02	0.03	0.011	0.019
0h08	0.076	0.019	0.057
0h14	0.12	0.065	0.055
0h20	0.16	0.039	0.121
0h26	0.19	0.050	0.140
0h32	0.22	0.063	0.157
0h38	0.23	0.081	0.149
0h44	0.24	0.102	0.138
0h50	0.23	0.130	0.100
0h56	0.22	0.159	0.061
1h02	0.225	0.181	0.044
1h08	0.23	0.204	0.026
1h14	0.25	0.220	0.030
1h20	0.26	0.237	0.023
1h26	0.27	0.250	0.020
1h32	0.28	0.261	0.019
1h38	0.29	0.274	0.016
1h44	0.30	0.285	0.015
1h50	0.31	0.296	0.014
1h56	0.315	0.304	0.011
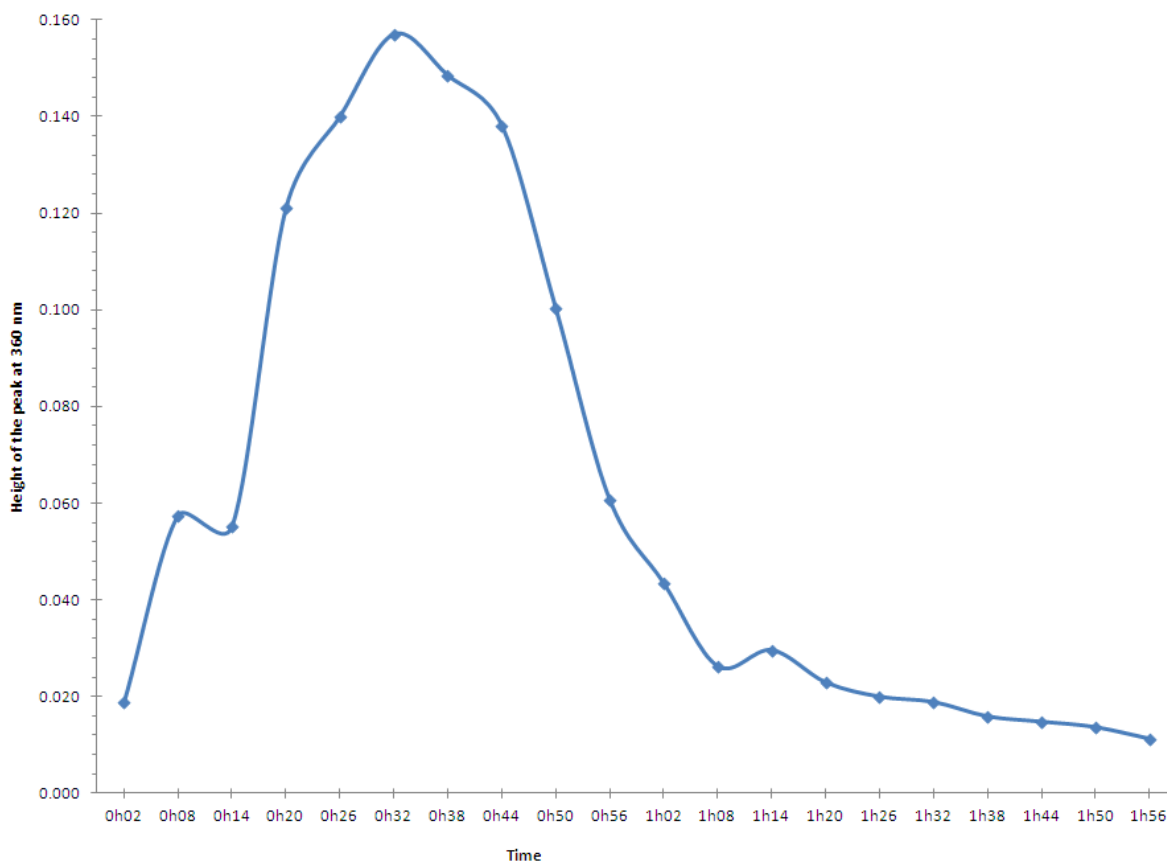
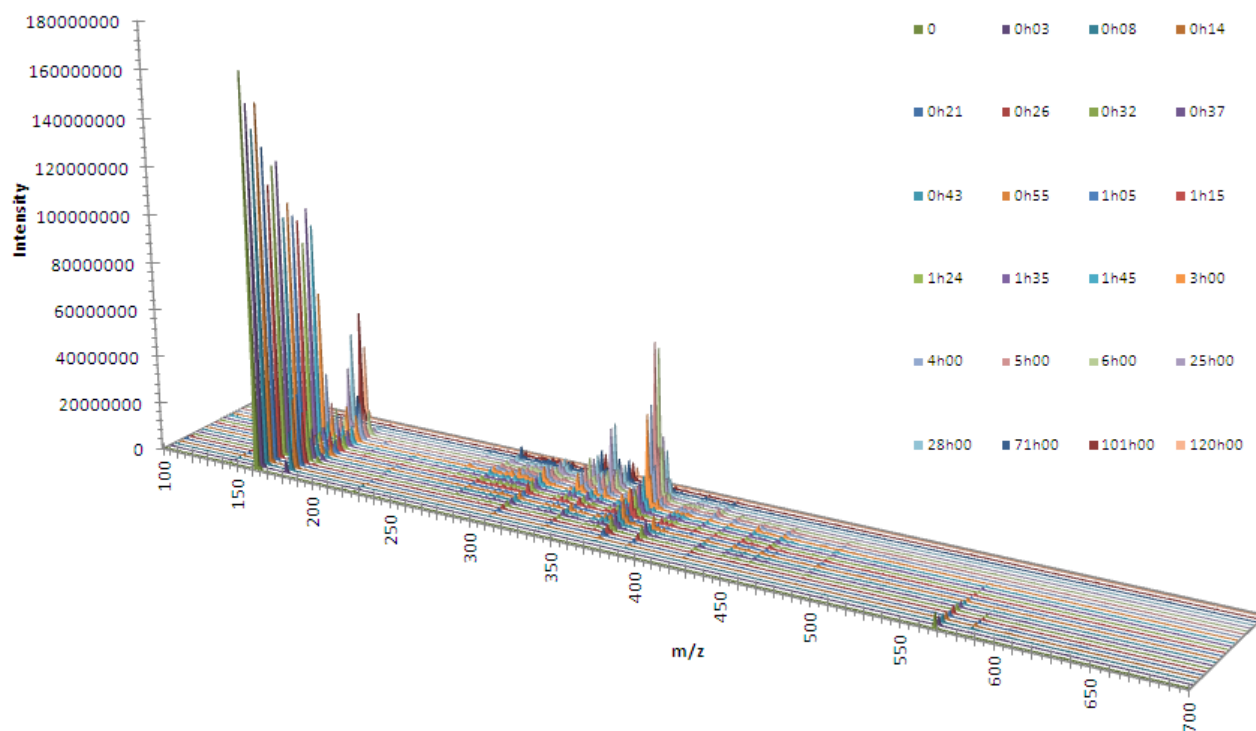**Figure S4.** Time evolution of the height of the peak at 360 nm.

Figure S5. Longer kinetics study of tetrabuthylammonium pertechnetate reacting with bis(trimethylsylil) sulfide ratio 1(Tc) – 200 (S) using electrospray ionization and mass spectrometry in negative polarity with 100 % acetonitrile carrier solvent.

4

Computational method for technetium.

Table S3. Transition energies and oscillator strengths for TcO_3S^- computed using time-dependent density functional theory (TD-DFT) at the B3LYP/SDD level of theory using a polarizable continuum model (PCM) for the acetonitrile solvent. The composition of individual excitations is also reported in terms of major one-electron transitions between the molecular orbital levels schematically represented in Figure 5. Major one-electron contributions to the bands are indicated in bold font.

Transition energy		Composition of major bands	Oscillator strength
[nm]	[eV]		
459	2.70	**(HOMO, H-1)→(LUMO, L+1)**	0.0014
365	3.40	**H-1→LUMO; HOMO→L+1** H-3→L+2	0.0702
342	3.63	**H-2→(LUMO, L+1)** (H-4, H-5)→(LUMO, L+1)	0.0029
303	4.09	**H-3→(LUMO, L+1)** (H-4, H-5)→(LUMO, L+1)	0.0014
292	4.25	**H-5→LUMO; H-4→L+1**	0.0028
273	4.55	**(H-4, H-5)→(LUMO, L+1)** H-6→(LUMO, L+1); H-3→(LUMO, L+1); H-2→ (LUMO, L+1); (HOMO, H-1)→L+2	0.0058
253	4.90	**H-1→L+3; HOMO→L+4** H-3→L+2	0.0125
250	4.96	**H-6→(LUMO, L+1)** (H-4, H-5)→(LUMO, L+1); (H-4, H-5)→L+2; H-2→ (L+3, L+4, L+5)	0.0089
214	5.80	**(HOMO, H-1)→L+5**	0.0267
211	5.88	**H-2→L+3; H-2→L+4** H-6→(L+4, L+5); (H-4, H-5)→L+3; H-4→L+2; H-4→ L+4, H-6→L+3; H-5→L+2, H-5→L+4,)	0.0080
204	6.08	**H-6→L+2; H-3→L+2**	0.0506
197	6.30	**H-3→(L+3, L+4)** H-5→ (L+3, L+4)	0.0018

187	6.64	(H-8, H-9)→(LUMO, L+1); H-7→(LUMO, L+1); H-6 →L+4; H-6→L+3; (H-4, H-5)→L+3; (H-4, H-5)→ L+4; H-3→L+4; H-3→L+3	0.0011
186	6.67	**H-6→L+2; H-1→L+7; HOMO→L+8** H-3→L+2	0.2244
183	6.78	**(HOMO, H-1)→L+6**	0.0072
181	6.86	**(HOMO, H-1)→(L+7, L+8)** (H-8, H-9)→(LUMO, L+1); H-7→(LUMO, L+1)	0.0114

Table S4. Transition energies and oscillator strengths for TcO_4^- computed using time-dependent density functional theory (TD-DFT) at the B3LYP/SDD level of theory using a polarizable continuum model (PCM) for the acetonitrile solvent. The composition of individual excitations is also reported in terms of major one-electron transitions between the molecular orbital levels. Major one-electron contributions to the bands are indicated in bold font.

Transition energy		Composition of major bands	Oscillator strength
[nm]	[eV]		
302	4.11	**HOMO→LUMO; (H-1, H-2)→L+1; H-5→L+1** (H-1, H-2)→LUMO; (H-3, H-4)→LUMO; (H-3, H-4) →L+1	0.012
249	4.98	**H-5→L+1; (H-3, H-4)→LUMO** (H-3, H-4)→L+1; HOMO→LUMO; (H-1, H-2)→L+1; (HOMO, H-2)→L+2; (H-1, H-2)→L+4; (HOMO, H-1) →L+3; (H-1, H-2)→LUMO	0.0173
209	5.94	**(HOMO, H-2)→L+2; (HOMO, H-1, H-2)→(L+3, L+4)** (H-4, H-5)→L+2; (H-3, H-4, H-5)→(L+3, L+4)	0.0079
177	7.01	**H-6→(L+3, L+4); (H-4, H-5)→L+2, (H-3, H-4, H-5) →(L+3, L+4); H-6→L+2** H-9→L+1; (H-10, H-11)→LUMO	0.0008
166	7.48	**H-9→L+1; (H-10, H-11)→LUMO; H-6→(L+3, L+4); H-6→L+2** (H-10, H-11)→(LUMO, L+1); (H-3, H-4, H-5)→L+5	0.0004
165	7.52	**(H-3, H-4, H-5)→L+5** (H-9, H-10, H-11)→(LUMO, L+1); (HOMO, H-1, H-2)→(L+6, L+7, L+8); (H-3, H-4)→L+5	0.0009

Solid state analysis on technetium.

We know that tetrabutylammonium pertechnetate is soluble in acetonitrile. So in order to see if the final solid still contained some pertechnetate unreacted, 40 mg of product was washed several times by acetonitrile. In a centrifuge tube, 5 mL of acetonitrile was added to the solid; the tube was shaken for one minute and then centrifuged for 2 minutes. The brown solution was removed and 5 mL of acetonitrile was added into the centrifuge tube. The previous supernatant was analyzed by UV-Visible spectroscopy and ESI/MS immediately. After the analysis, the solid was again centrifuged for 2 minutes. The yellow solution was removed and 5 mL of acetonitrile was added to wash again the solid. The solid was washed 4 times in total, the last solution was colorless, and the three first solutions were analyzed by UV-Visible spectroscopy and ESI/MS. In order to dry the solid, the product was washed 3 times with diethyl ether (5 mL each) followed by 3 more washes of hexane (5 mL each). The solid was left to dry overnight in the back of the hood, and we collected 31.5 mg of black solid.
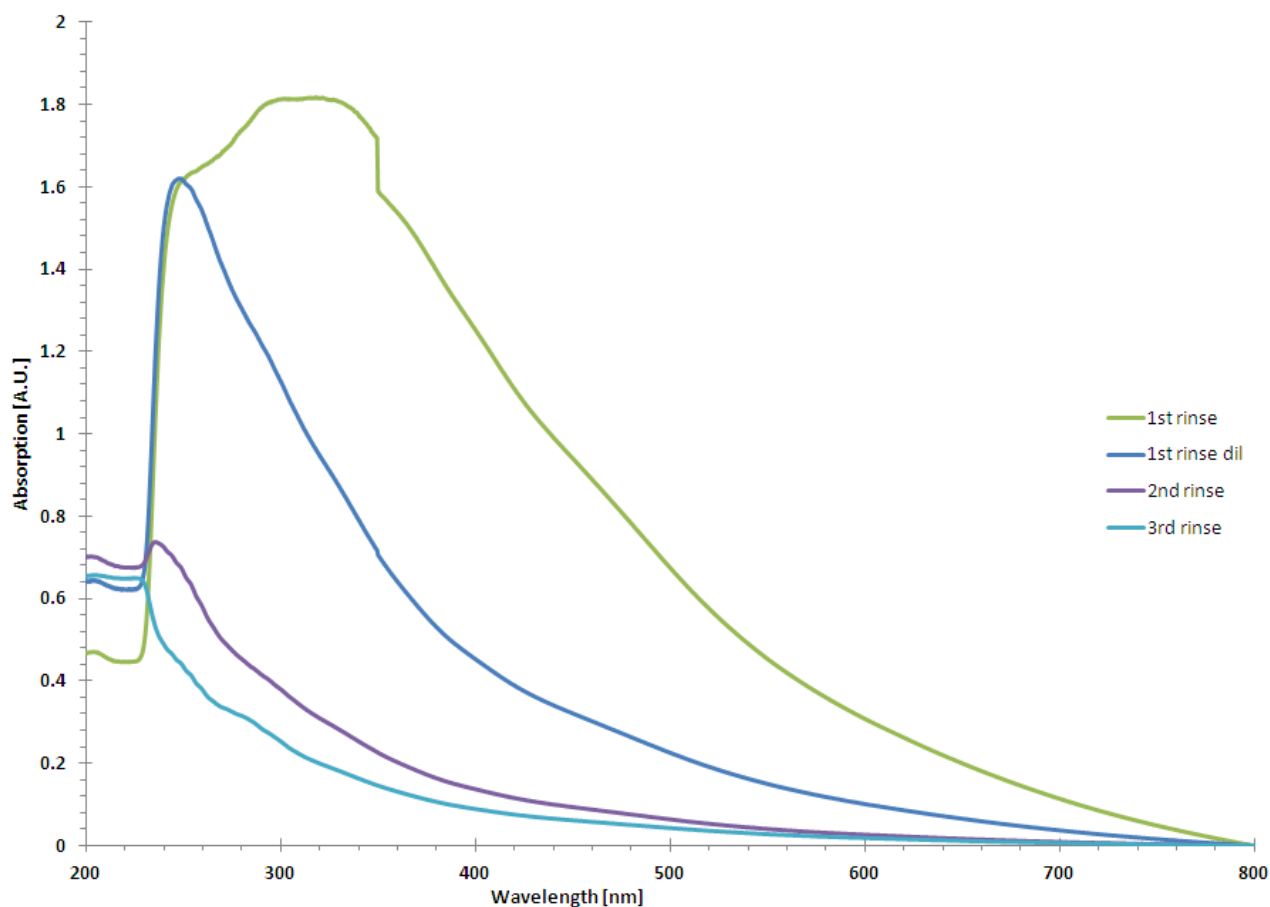

Figure S6. UV-Visible spectra of the acetonitrile supernatants obtained after each wash, with a baseline correction of acetonitrile.
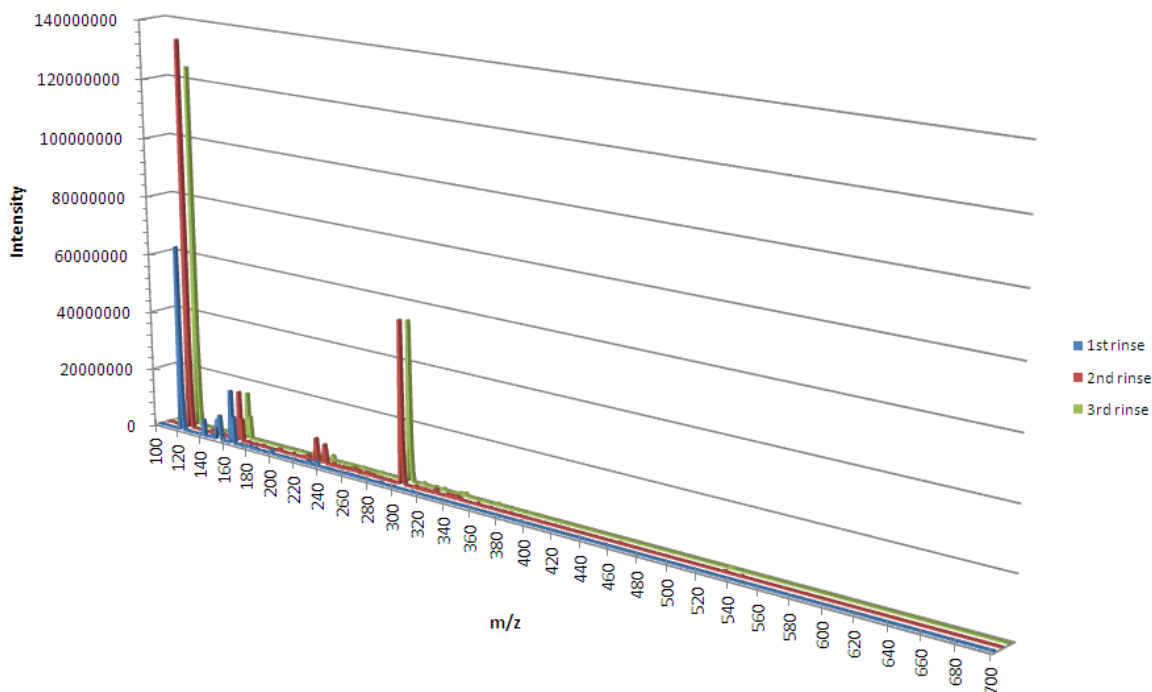
Figure S7. ESI/MS spectrum of acetonitrile supernatants obtained after each wash in negative polarity.
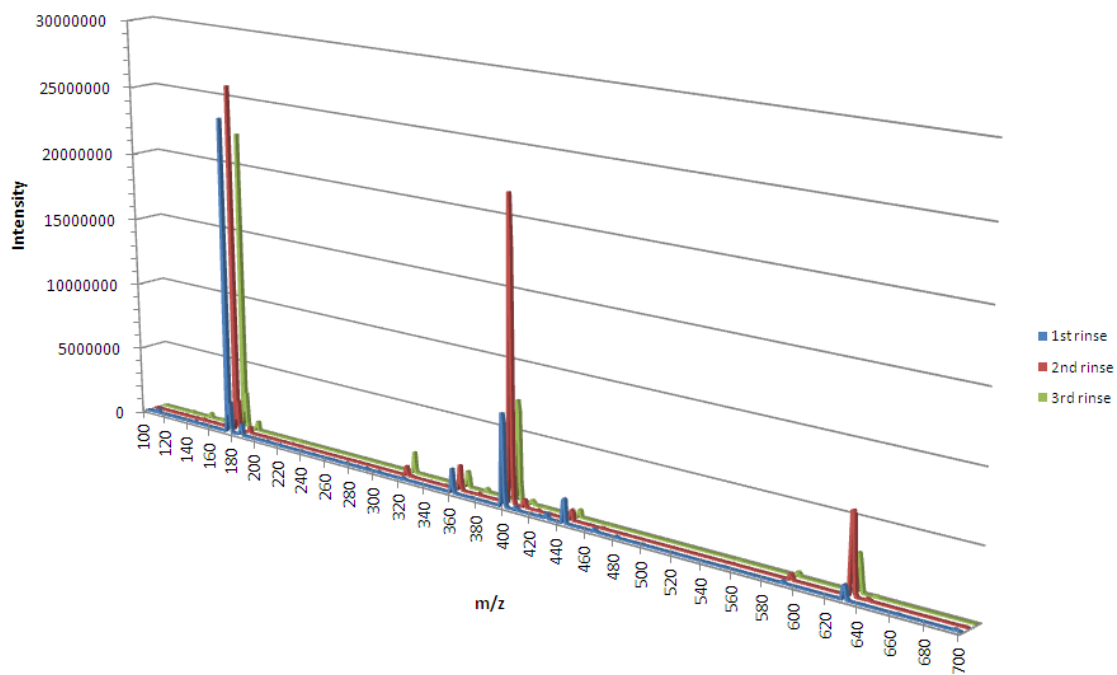

Figure S8. ESI/MS spectrum of acetonitrile supernatants obtained after each wash in positive polarity.

The exact determination of every peak in the spectra was challenging. However, this experiment was designed to analyze the solution from large scale's solid wash. Thus, the acetonitrile wash can contain different components; some solvent molecules from previous washes, starting compounds or

some oxo-sulfide technetium polymers soluble in acetonitrile. The goal of this analysis was to know if any technetium starting compound was still present in the solid that could explain the presence of oxygen. In the spectra we do not observe any peak at m/z = 163 (in negative polarity, Figure 7) and m/z = 242 (in positive polarity, Figure 8), which means that we do not have any pertechnetate negative ion or tetrabutylammonium positive ion. As a result, we can say that in the spectra the lower mass-to-charge ratio peaks corresponds to impurities in the system since their masses are lower that pertechnetate itself, while higher mass peaks can be correlated to some technetium polymers.

We know that TcO_2 and Tc (IV) compounds are soluble in concentrated hydrochloric acid. So in order to see if the final solid contains some Tc (IV), 22 mg of product was put into 5 mL of HCl for 5 days. In a centrifuge tube, the 5 mL of solution was removed. Then the solid was washed with various solvents. First 5 mL of acetonitrile was added to the solid to remove the hydrochloric acid; the tube was shaken for two minutes and then centrifuged for 3 minutes. The brown solution was removed and 5 mL of acetonitrile was added into the centrifuge tube. The solid was washed 4 times in total, the last solution was colorless. In order to dry the solid, the product was washed 3 times with toluene (5 mL each) followed by 3 more washes of hexane (5 mL each). The solid was left to dry overnight in the back of the hood, and we collected 9.7 mg of really fine black powder.
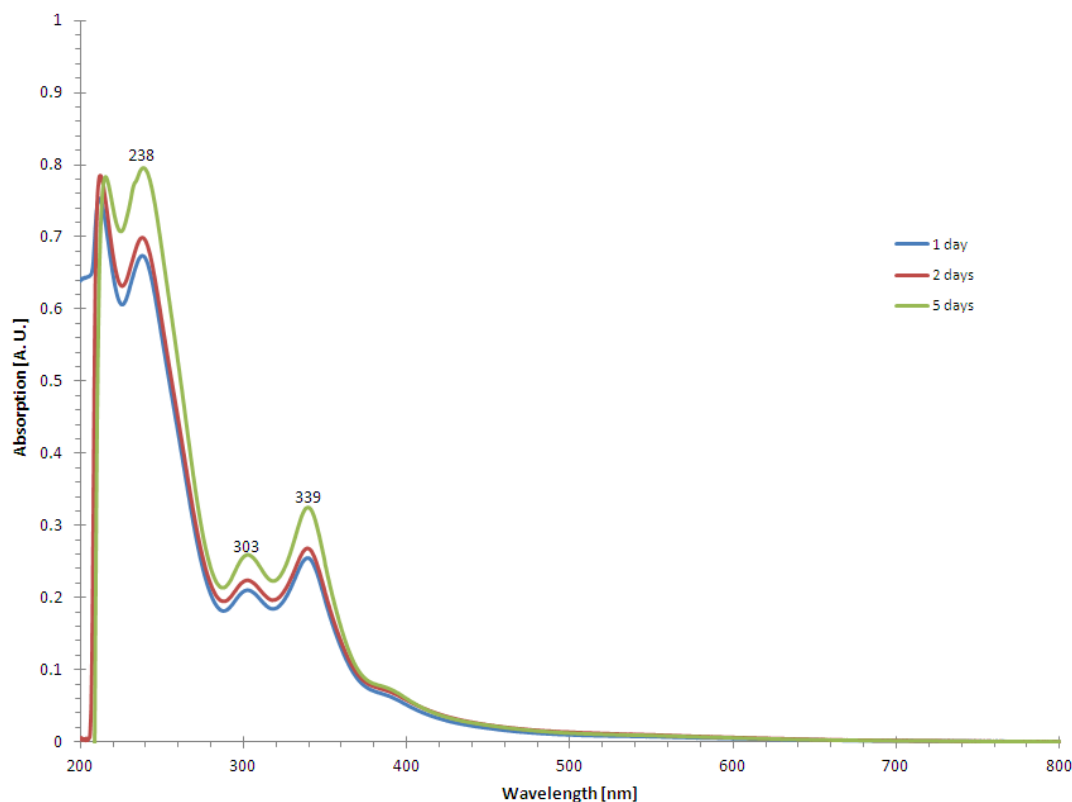

Figure S9. UV-Visible spectra of the HCl concentrated solution diluted by 50 over time, with a baseline correction of HCl concentrated.

Table S5. From the Beer Lambert equation (Absorbance = $\varepsilon.c.l$), determine the $TcCl_6^{2-}$ concentration in solution. The absorbance value is obtained from the UV-Visible data, the literature[6] gives ε (338 nm) = 10600 $mol^{-1}.L.cm^{-1}$, $l = 1$ cm, thus the concentration can be calculated:

Time	Absorbance [A. U.] at 338 nm	Concentration [$mol.L^{-1}$]
1 day	0.255	2.406×10^{-5}
2 days	0.268	2.528×10^{-5}
5 days	0.325	3.062×10^{-5}

We can conclude that some TcO_2 or Tc (IV) dissolved into the hydrochloric concentrated acid solution over time.

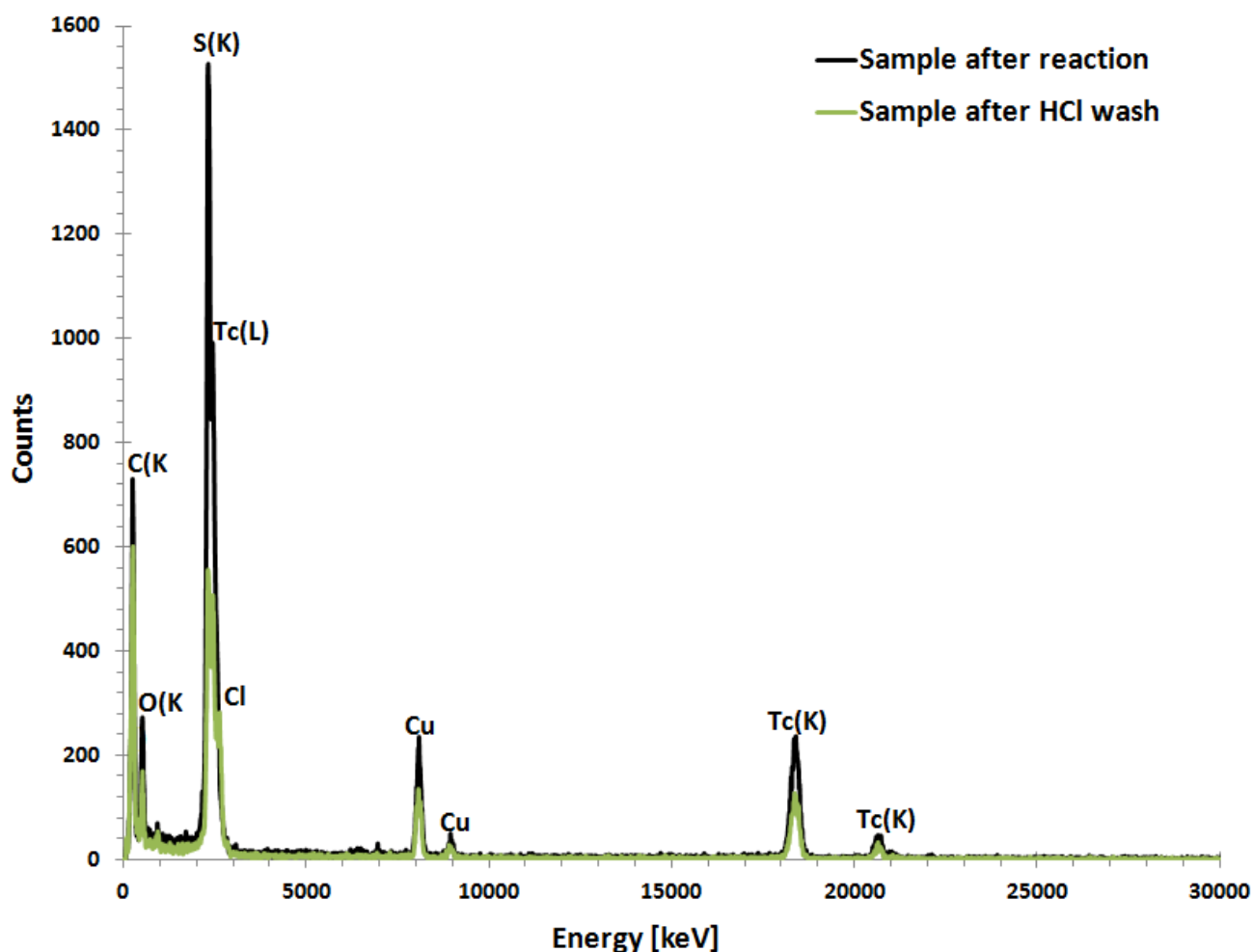The different EDX observed for the different solid analyzed are compared in the Figure S10.

Figure S10. Comparison of the EDX spectra for the two samples analyzed.

Table S6. On each EDX spectrum a qualitative analysis was performed in order to evaluate the atomic/weight percentage of oxygen, sulfur and technetium. A mean of the values determined on 6 or 7 EDX spectrum for each sample was calculated for each element.

Element	Correction	k-factor	Sample after reaction			Sample after HCl dissolution		
			Weight%	Atomic%	Uncertainty%	Weight%	Atomic%	Uncertainty%
O(K)	0.514	2.014	6.139	18.370	0.092	9.660	30.507	0.108
S(K)	0.911	1.095	35.162	52.759	0.146	19.476	31.213	0.114
Tc(K)	0.997	4.589	58.699	28.871	0.338	70.861	38.280	0.354

References:

1 D. V. Partyka and R. H. Holm, *Inorg. Chem.*, 2004, **43**, 8609.

2 (a) A. Müller, B. Krebs, W. Rittner, M. Stockburger and Ber Bunsenges, *Phys. Chem*, 1967, **71**, 182; (b) A. Müller, E. Diemann, F. Neumann and R. Menge, *Chem. Phys. Lett*, 1972, **16**, 521.

3 A. Carrington, D. Schonland and M. C. R. Symons, *J. Chem. Soc. London*, 1957, 659.

4 A. Müller, E. Diemann, R. Joste and H. Bögge, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 934.

5 http://www.sisweb.com/referenc/source/exactmaa.htm, visited 07-10-11.

6 K. Schwochau, Technetium: Chemistry and Radiopharmaceutical Applications, Wiley-VCH: Weinheim, Germany, 2000.