



Speciation of Technetium in Sulfuric Media. Effect of α - Radiations from the Arronax Cyclotron.

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Chemistry of Technetium at Subatech, Nantes, France.



Subatech at School of Mines



- Chemistry of Tc in the context of radioactive waste disposal
- Tc speciation in aqueous media (Cl⁻, TFMS⁻, SO₄²⁻, CO₃²⁻...)
- Effect of alpha, protons and gamma radiations on Tc chemistry

7 Thesis on Technetium chemistry since 1996:

K. Bensaïd, L. Vichot, F. Poineau, X. Liu, I. Ilorens, N. Vongsouthi, I. Denden (2010)

Introduction

I. Experimental methods

II. Speciation of reduced Tc species in sulfuric acid

- 1- UV-visible spectroscopy
- 2- XAFS spectroscopy

III. Effect of alpha-radiations on Tc speciation in sulfuric acid

- 1- UV-visible spectroscopy

Conclusions and future works

Introduction

Group VII metals are used in catalysis and biomedical applications.

- $[\text{ReO}_3]^+$ complexes for catalysis and $^{99\text{m}}\text{Tc}$ for radio-imaging

Technetium studies in acidic conditions relevant to fundamental chemistry

- Initial study in $[\text{H}_2\text{SO}_4]$

Speciation of heptavalent technetium in sulfuric acid* → German, K. Monday

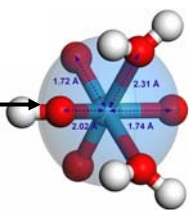
Poster 1.p10

- Dissolution of KTcO_4 in $[\text{H}_2\text{SO}_4] > 12 \text{ M}$ leads to $\text{TcO}_3(\text{H}_2\text{O})_2\text{OH}$

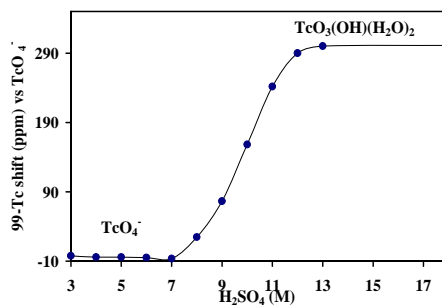
- $\text{TcO}_3(\text{H}_2\text{O})_2\text{OH}$ seems to be very sensitive to reduction



KTcO_4 in 12 M H_2SO_4

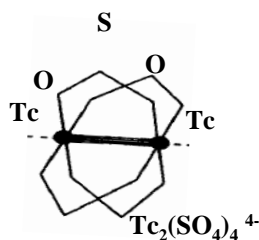
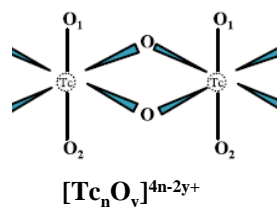


$\text{TcO}_3(\text{H}_2\text{O})_2\text{OH}$



Speciation of reduced Tc species in sulfate not well studied

- Polymeric Tc(IV) in 0.01 M H_2SO_4 : $[\text{Tc}_n\text{O}_y]^{4n-2y+}$
- Quadruple bonded Tc(III) dimer in concentrated $[\text{H}_2\text{SO}_4]$: $\text{Tc}_2(\text{SO}_4)_4^{4-}$
- No monomeric Tc complexes coordinated to sulfates characterized



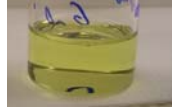
Goal :

- Investigate the formation of reduced Tc-sulfate complexes from the chemical and radiochemical reduction of $\text{TcO}_3(\text{H}_2\text{O})_2\text{OH}$

I. Experimental methods

Preparation of solution

Dissolution of KTcO_4 in 12-18 M H_2SO_4



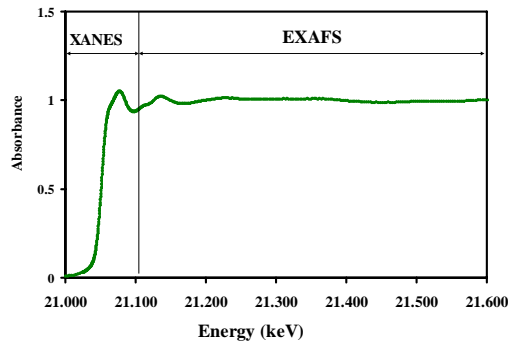
MeOH →

Formation of Tc reduced species
• Reduction with methanol



Spectroscopic methods

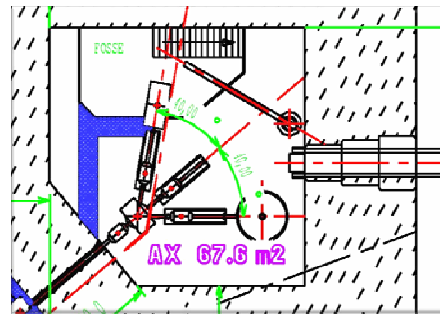
Characterization of Tc reduced species by UV-visible and XAFS spectroscopy



XANES → Local geometry and oxidation state

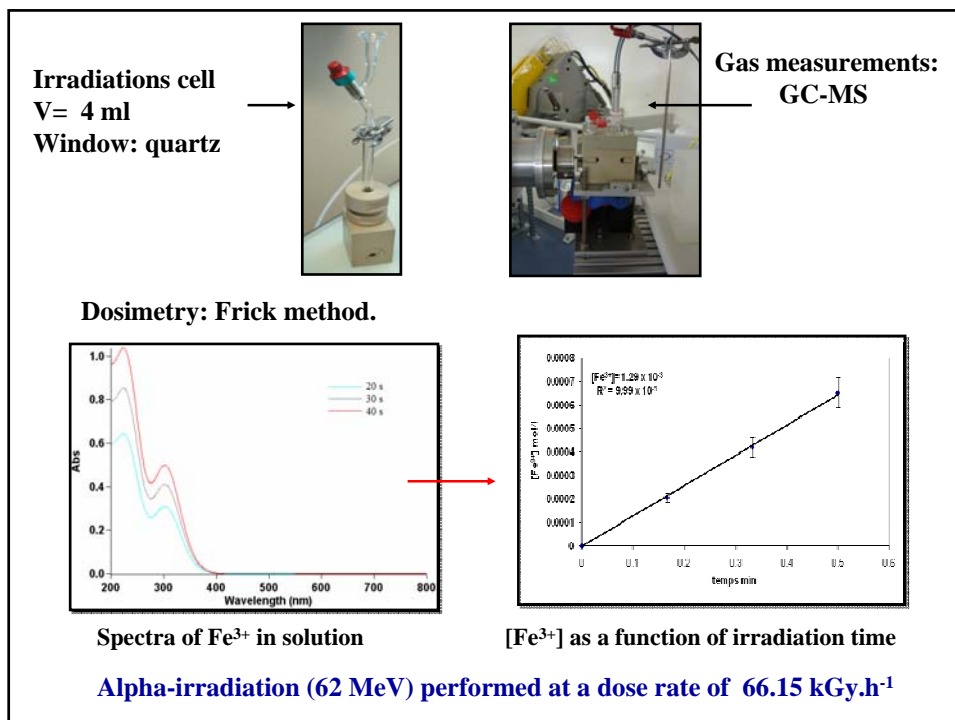
EXAFS → chemical and structural parameter

Experiments under alpha-radiations



ARRONAX cyclotron, Nantes, France:

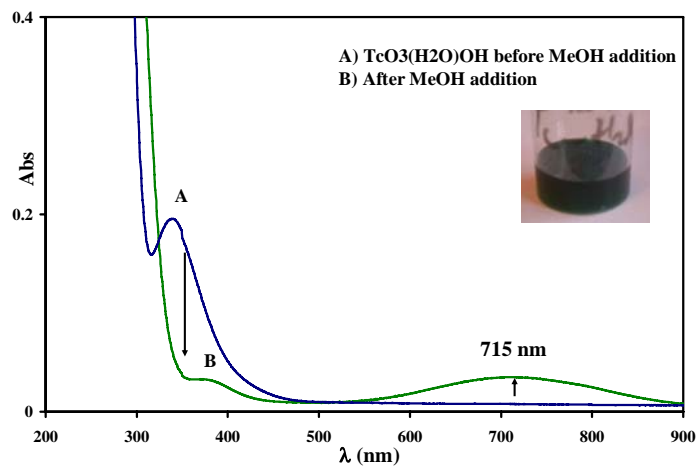
- High energy (70 MeV for alpha)
- High intensity (750 μA for accelerated protons)



II. Speciation of reduced Tc species in sulfuric acid

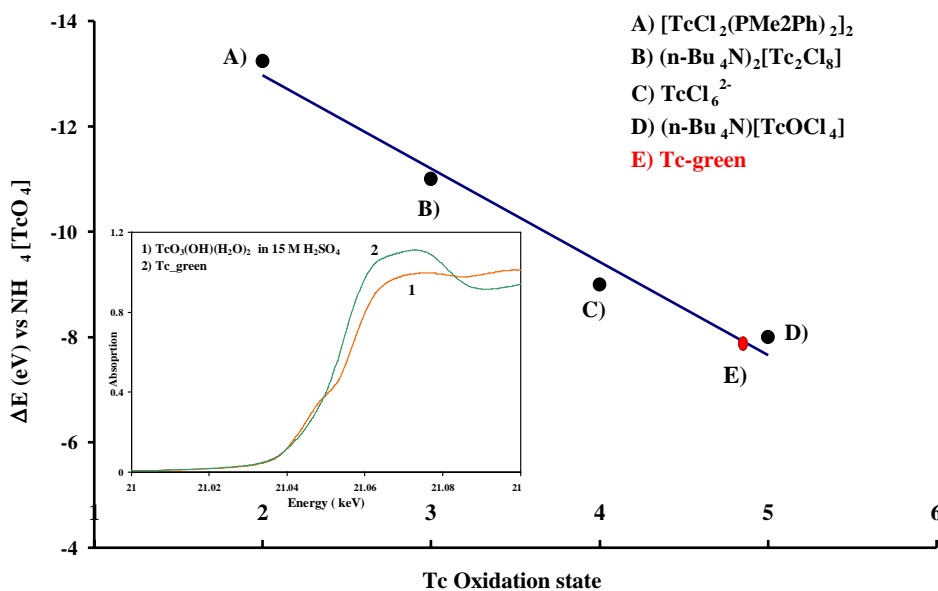
1. UV-visible spectroscopy

Reduction of $\text{TcO}_3(\text{H}_2\text{O})_2\text{OH}$ (Tc: 10 mmol, 15 M H_2SO_4) by MeOH (10 μl)
 ·Fast reduction: formation of a green solution (“Tc-green”)



New specie “Tc-green”: bands at 390 nm and 715 nm
 Similar spectra obtained between 12 M and 18 M $[\text{H}_2\text{SO}_4]$
 No reaction observed below 12 M $[\text{H}_2\text{SO}_4]$

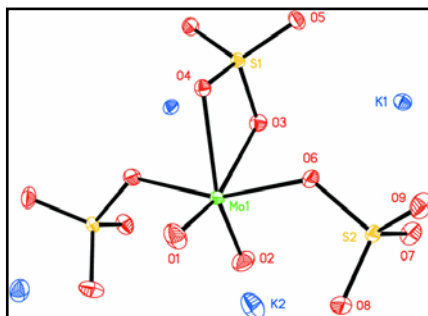
2. XANES



·Edge position (21055) eV of Tc-Green consistent with Tc(V)

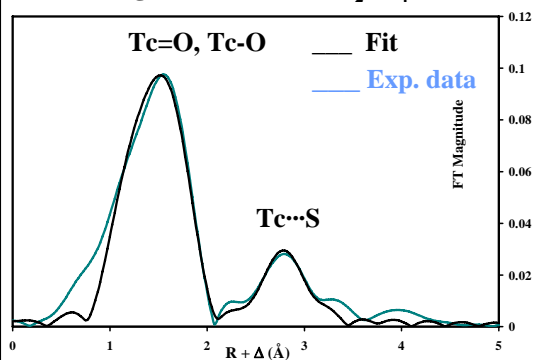
3. EXAFS

Adjustment of the k^3 -EXAFS spectra of Tc-green using the scattering calculated in $K_4MoO_2(SO_4)_3$



Mo=O1,2: 1.688 Å
 Mo-O6: 2.036 Å
 Mo-O3: 2.266 Å
 Mo-O3: 2.183 Å
 Mo...S1: 2.954 Å (S bidentate)
 Mo...S2: 3.228 Å (S monodentate)

FT of green Tc in 15 M H_2SO_4



	Structural parameter		
	C.N	R (Å)	σ^2
Tc=O	0.9	1.60	0.0002
Tc-O	4.8	2.04	0.003
Tc-S	1.9	3.23	0.002

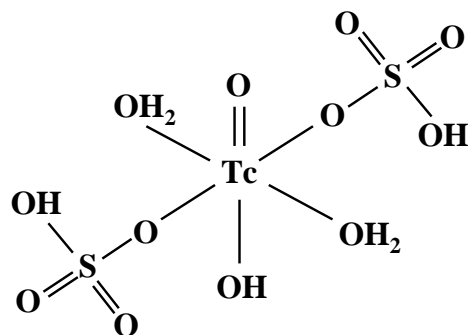
Results of EXAFS adjustment

- Monomeric octahedral complex
- One oxygen atom at 1.60(2) Å: Tc=O; characteristic of Tc(V)
- Five oxygen atoms at 2.04(2) Å: Tc-O; Tc-OH, Tc-H₂O, Tc-O(S)
- Two sulfur atoms at 3.23(3) Å: Tc...S; two monodentate sulfate

In 15 M [H₂SO₄] : bisulfate anion (HSO₄⁻) is predominant specie (~ 12 M)

· Bisulfate anion in monodentate mode

· The formula TcO(HSO₄)₂(H₂O)₂(OH) is proposed



Structure proposed for Tc-Green

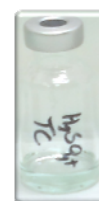
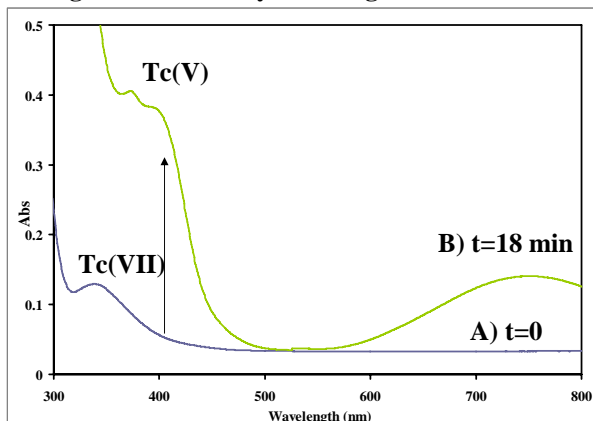
Formation mechanism proposed:



III. Effect of alpha-radiations on Tc speciation in sulfuric acid

UV-visible spectroscopy

Irradiation (18 minutes) of a 4 mmol $\text{TcO}_3(\text{OH})(\text{H}_2\text{O})_2$ in 18 M $[\text{H}_2\text{SO}_4]$
 → Change of color from yellow to green



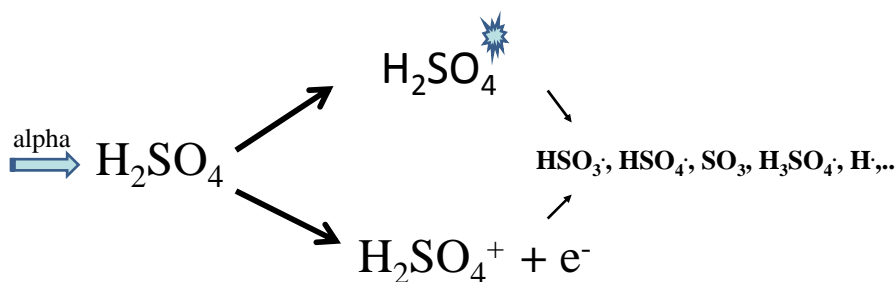
after irradiation

UV-visible spectra of $\text{TcO}_3(\text{OH})(\text{H}_2\text{O})_2$ in 18 M $[\text{H}_2\text{SO}_4]$
 before (A) and after 18 min of irradiation (B)

→ Spectra similar to $\text{TcO}(\text{HSO}_4)_2(\text{H}_2\text{O})_2(\text{OH})$

Radiolytical reduction of Tc(VII) to Tc(V) by radicals

Radicals formed during alpha-radiation of concentrated sulfuric acid :



Very few study on alpha- radiolysis of concentrated $[\text{H}_2\text{SO}_4]$
 Need further experiment to determine reduction mechanism
 · Gas measurement ...

Conclusions and Future works

Heptavalent technetium very sensitive to reduction between 12 M to 18 M [H₂SO₄]
·Reduced to Tc(V) by MeOH

EXAFS spectroscopy consistent with Tc^VO(HSO₄)₂(H₂O)₂(OH)

Heptavalent technetium is unstable under α-radiation in 18 M H₂SO₄
·Reduced to Tc^VO(HSO₄)₂(H₂O)₂(OH) by [H₂SO₄] radiolysis products

→ Synthesis of a Tc^VO(HSO₄)₂(H₂O)₂(OH) crystal for XRD determination

→ Determination of Tc(VII) reduction mechanism under alpha-radiation
Gas measurement during [H₂SO₄] irradiation

→ Speciation of heptavalent and reduced technetium in triflic acid

Acknowledgments

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Questions