

Journée PRACITS 1999

Villeneuve-les-Avignon 17-18 fevrier 2000

***Impact of Sulphide on the
Environmental Behavior of Tc-99 :
Reaction Kinetics with Pertechnetate ;
Growth and Coagulation of Tc_2S_7 Colloid***

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An excellent book issued in December 1999:

Chemical Thermodynamics of Technetium

J. A. Rard, M.H. Rand, G. Anderegg, H. Wanner

➤ **It covers most items being important for Tc environmental studies**

➤ **Indicates the remaining problems and among these pointing out the one as:**

➤ **“... 7. Either $\text{TcS}_2(\text{s})$ or $\text{Ts}_2\text{S}_7(\text{s})$ could potentially form as a solubility-limiting phase for Tc in ground waters...
Experimental thermodynamic data are required to replace the rather uncertain estimated values for these compounds”.**

/J.Rard/

- Ordering <http://www.nea.fr/html/dbtdb/cgi-bin/order.pl>

- Publisher: North-Holland/Elsevier Science B. V., Amsterdam ISBN: 0-444-50378-1 Publishing year: 1999

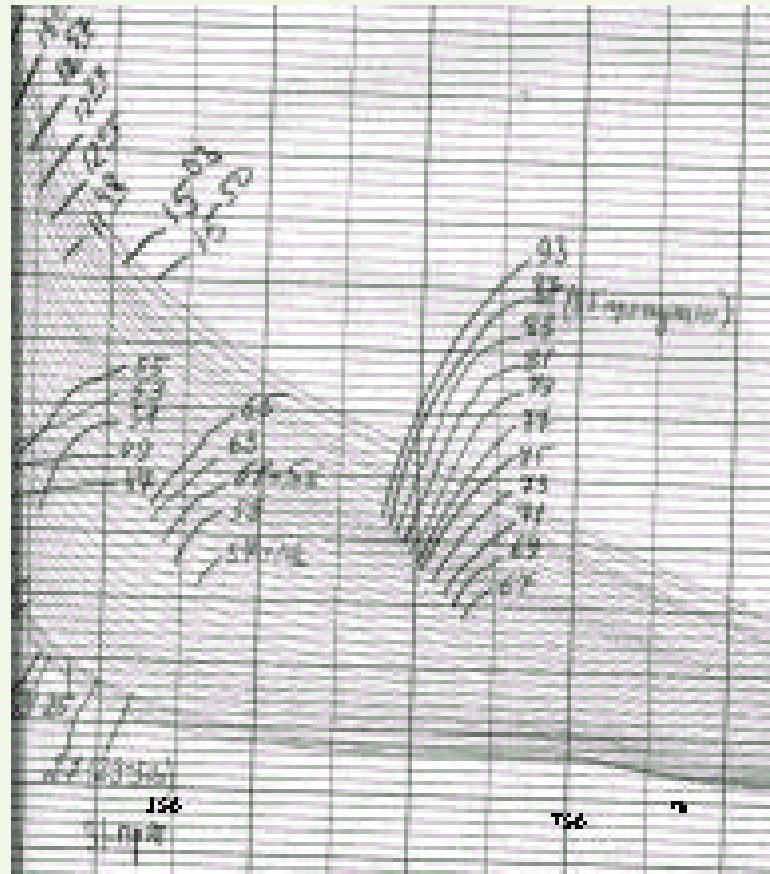
- **22+544 pages**

INSTRUMENTATION

CHEMICAL PREPARATION and SAMPLE TREATMENT

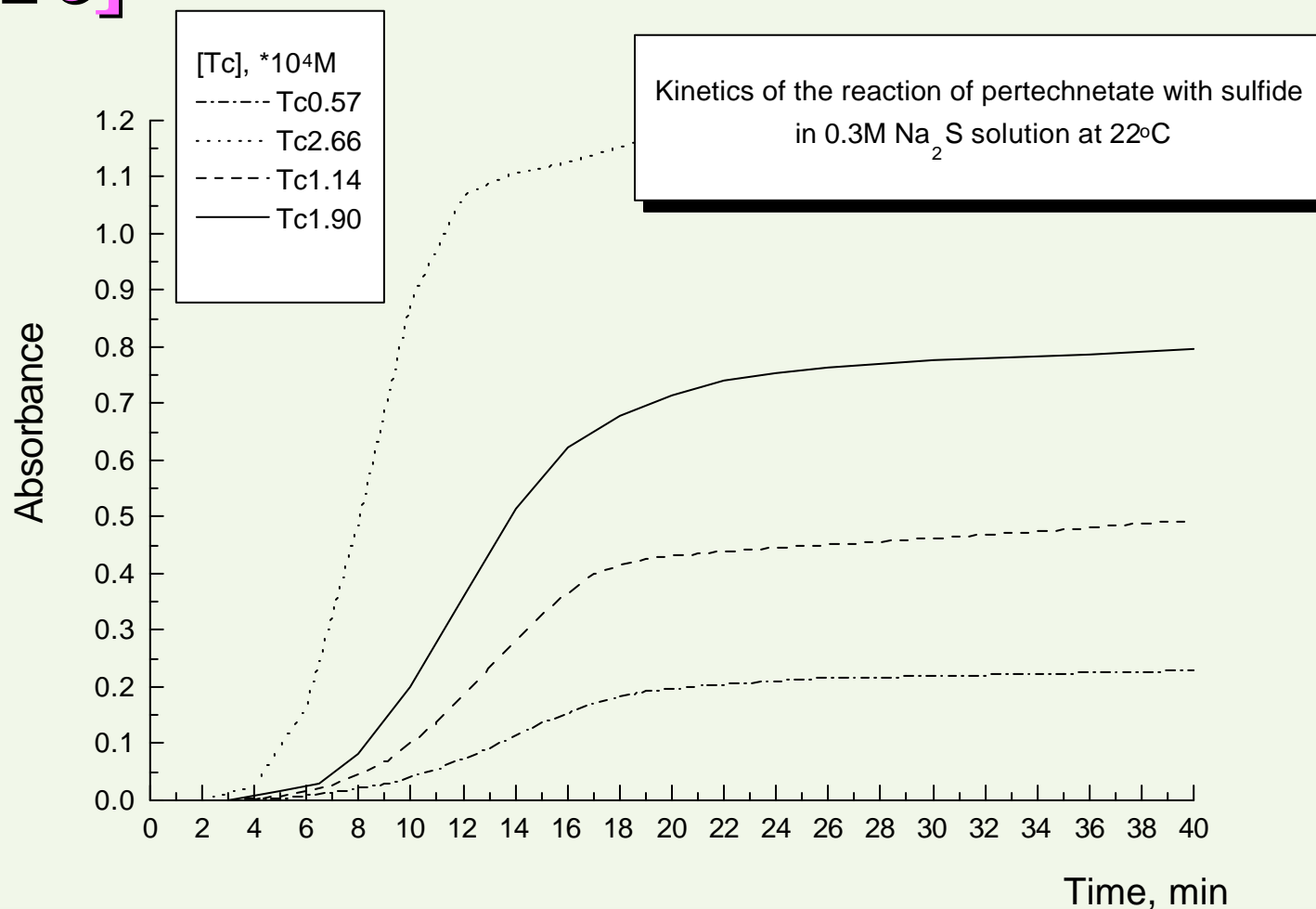
- Shimadzu model UV-3100 PC UV-Vis-NIR spectrophotometer (Japan)
- ***b*-counting** in Ready-Gel^ä scintillation cocktail (Beckman, USA) at Beckman LS6500 liquid scintillation counter
- Centrifuge MPW-21 (Poland): 0 - 15000 *rpm*
- Microfilterfuge tubes (RAININ Instr.Co) with 30000 NMWL ultrafiltration membranes
- All chemicals were of analytical grade
- Particle Size Speciation:
 - Sedimentation,
 - centrifuging at 8000 rpm
 - and ultrafiltration
- Media: Na₂S solutions
 - made always from freshly recrystallized Na₂S*9H₂O
 - it provide with buffer effect on solution *pH*
 - it reduces the sulfide loses in long - term experiments compared to H₂S

Experimental spectrum of Tc_2S_7 formation in the TcO_4^- reaction with Na_2S

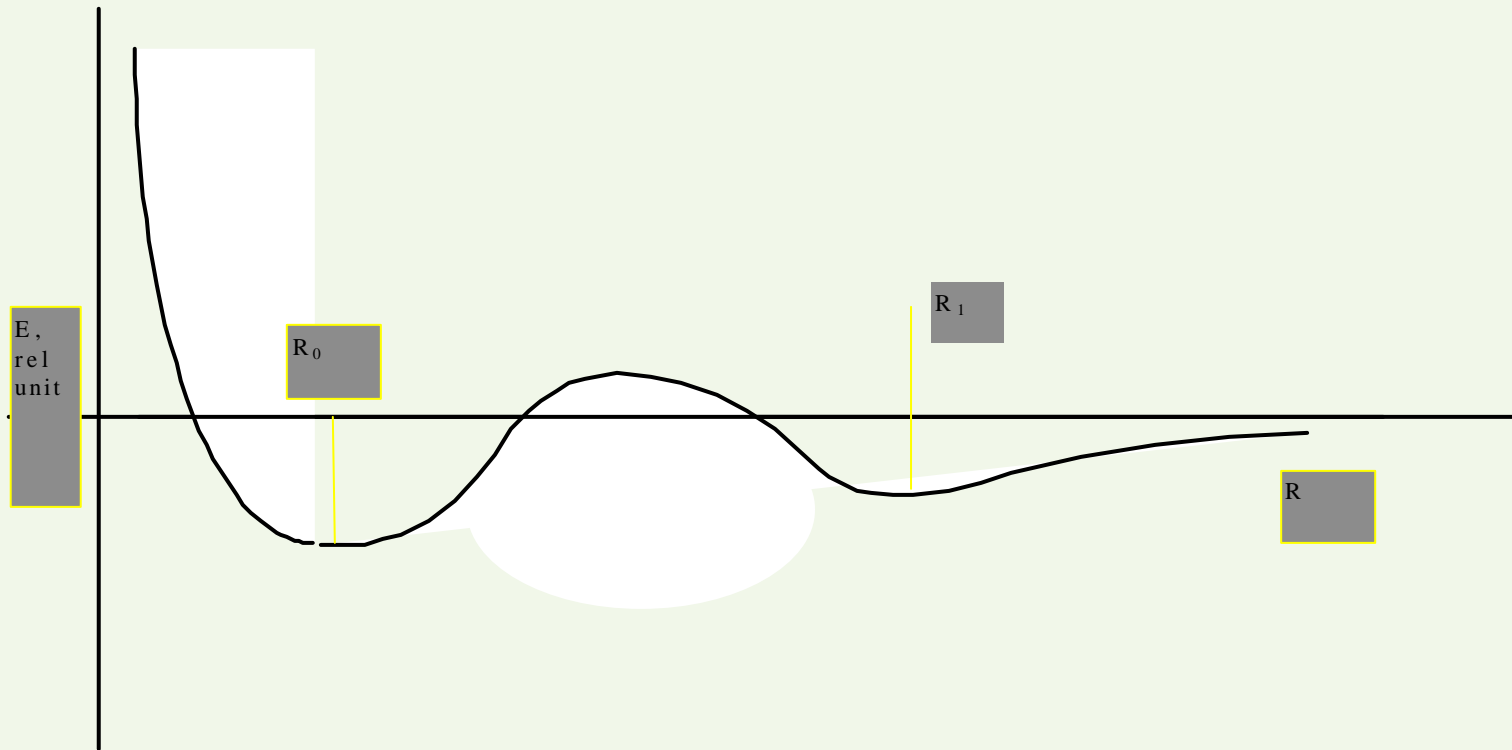


- UV-band is masked by the reagents (TcO_4^- and Na_2S)
- Vis-spectrum presents no bands but only shoulders
- The shoulders at 350 nm and 750 nm were used for analyses (with corresponding intensity corrections)

Absorbances at 350 and 750 nm shoulders follow the linear dependence on [Tc]

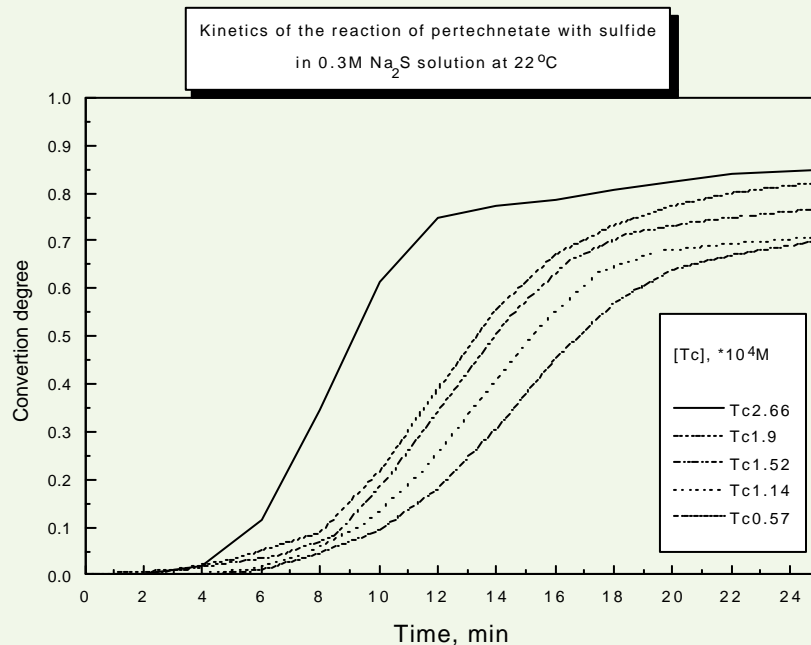


Colloid stability results from repulsion zone existing for certain particles nature, sizes and intra-particle distances



□ *Induction period of the reaction of pertechnetate with Na_2S varies from 4 to 100 minutes depending on the concentration of reagents, pH and T*

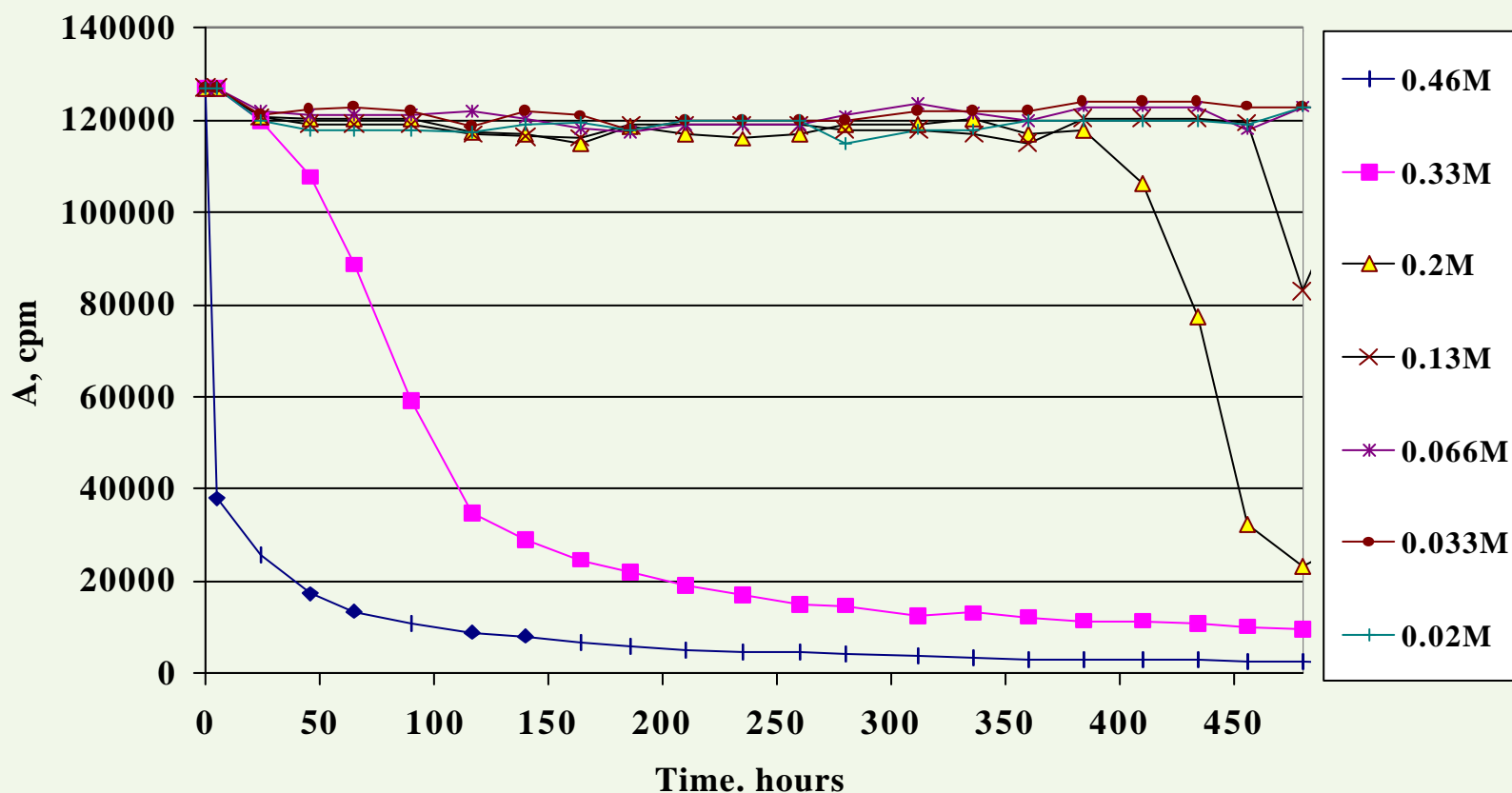
Reaction of pertechnetate with Na_2S is completed within one to ten hours depending on the concentration of reagents



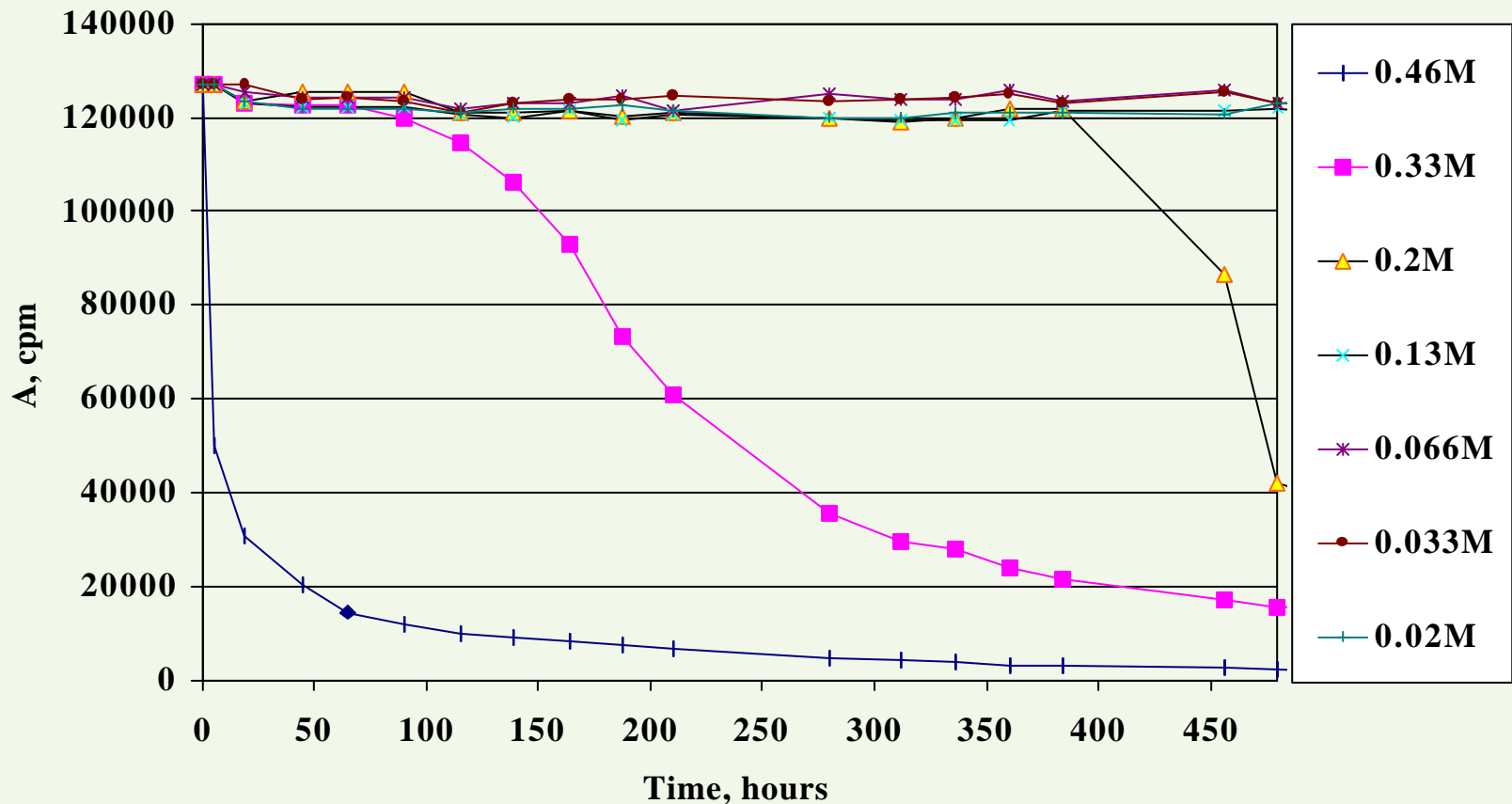
- *Reaction is fast if compared to Tc_2S_7 sedimentation (under most conditions) due to colloid formation*

Tc₂S₇ separation by centrifuging at 8000 r.p.m.

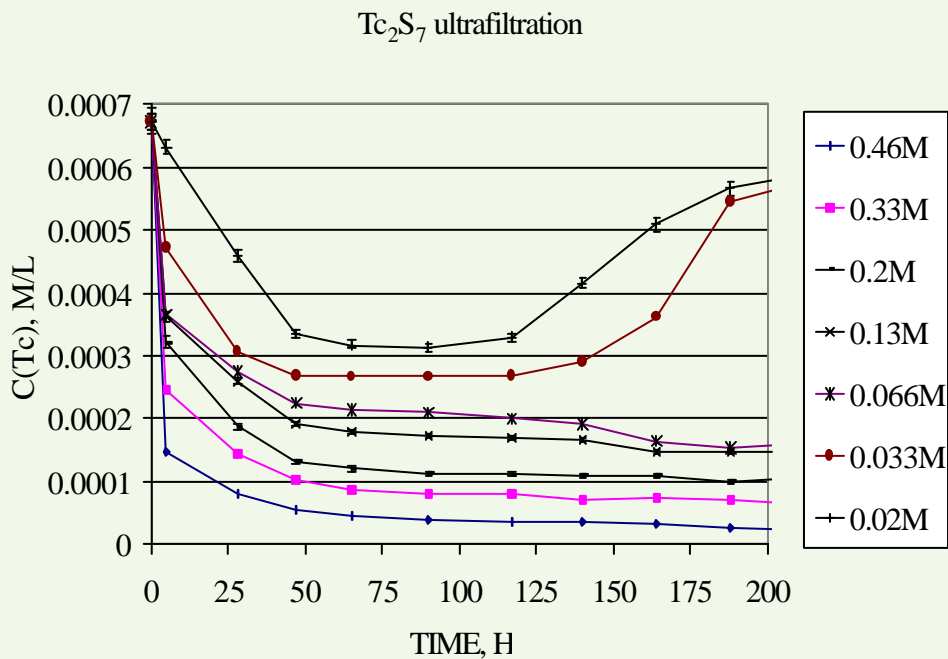
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Tc₂S₇ separation from solution by spontaneous sedimentation



Tc_2S_7 colloid ultrafiltration



- Formation of colloidal Tc_2S_7 is completed in 50 hours under studied conditions
- $[Tc]$ in the solution from 50 to 150 hours presents most likely the solubility of Tc_2S_7
- Longer times give additional information on several reactions occurring in the system (to be studied by EXAFS at ESRF/ROBL in the next year)

Tc₂S₇ Solubility in Na₂S Solutions

Solubility Tc₂S₇ in Na₂S solutions

