

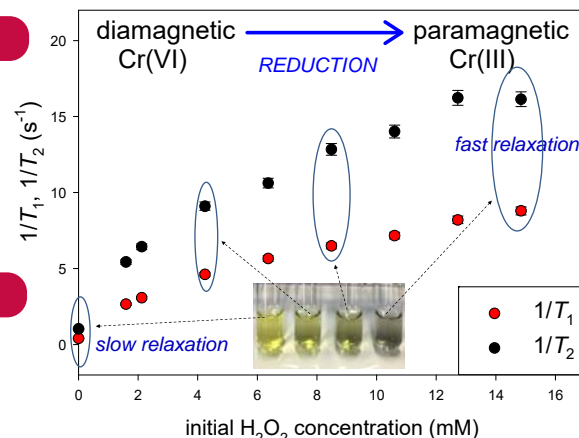
The evolution of Nuclear Magnetic Resonance relaxation rates of water protons is used to follow the reduction of diamagnetic Cr(VI) into paramagnetic Cr(III) by different reductants in different buffers. Detailed results can be found in ¹

1. Why reducing Cr(VI) into Cr(III) ?

- Cr(VI) is released in water by different industries (tanning, electroplating...)^{2,3},
- Cr(VI) is toxic for fauna and flora at low concentration (0.1 mg/ml),
- Cr(III) is an essential nutrient, only toxic at very high concentrations,
- ⇒ To reduce the toxicity of Cr(VI) in water: reduction to Cr(III) !
- Different possible reducing agents: H₂O₂ (pH < 5), ascorbic acid, zerovalent aluminum.

2. Why can NMR relaxometry be used ?

- Cr(VI) = full electronic orbitals → diamagnetic → no influence on water relaxation,
- Cr(III) has 3d unpaired electrons → paramagnetic → shorten water protons T₁ and T₂,
- ⇒ During the reduction, [Cr(III)] ↑ and 1/T₁ and 1/T₂ ↑ proportionally,
- ⇒ Nondestructive follow-up of reduction (without addition of chemical markers)^{4,5}
- Increase of 1/T₁ and 1/T₂ really proportional to [Cr(III)] ?
- ⇒ Independent measurement of remaining [Cr(VI)] by direct spectroscopy,
- Does it depend on the reductant ? Is there an influence of the reaction mixture?



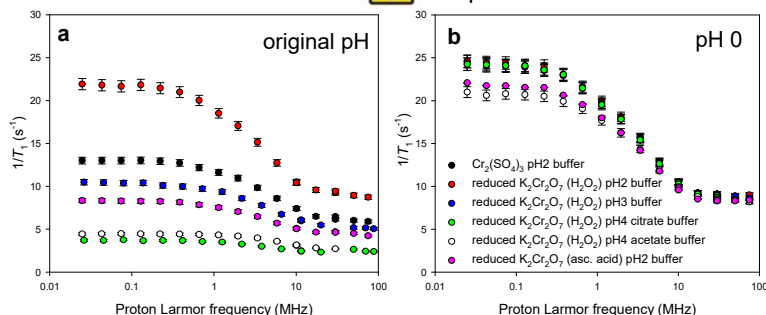
Sketch of a reduction experiment: increasing amounts of H₂O₂ are added to a series of similar K₂Cr₂O₇ solutions to achieve different partial reductions. The relaxation rates increase with [Cr(III)] of the reduced solutions.

3. Reduction of K₂Cr₂O₇ solutions by H₂O₂

- In pH2 KCl/HCl, pH3 NaCl/Glycine/HCl and pH4 sodium acetate/acetic acid buffers,
- Initial [Cr(VI)]=1.5 mM, initial [H₂O₂] ranging from 0 to 15 mM, T=22°C,
- T₂ measured by CPMG, T₁ by saturation recovery, B₀ = 0.68 T,
- 👍 correlation between 1/T₁ and 1/T₂ and remaining [Cr(VI)] measured by spectroscopy → seems to work for all buffers (~ for pH4),
- If reduction not too fast, kinetics can be studied in a single tube with T₂,
- Similar results at pH2 with ascorbic acid as reductant,
- ⚠️ Final 1/T₁ and 1/T₂ values depend on the buffer used and on the reductant.

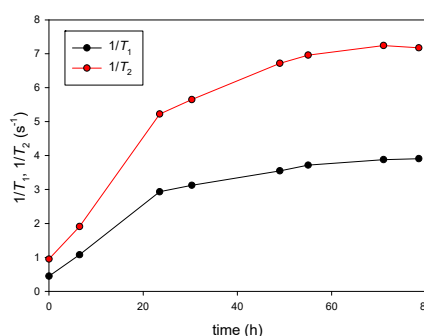
4. Influence of the reaction mixture: Complexation of Cr(III) ions

- Cr(III) ions can be complexed by molecules present in the solution: -glycine, acetate and citrate (from buffer), ascorbic acid (reductant),
- ⇒ Modification of the number of coordinated H₂O (q),
- ⇒ Modification of inner sphere relaxivity caused by Cr(III),
- ⇒ Different relaxation rates for the different reduced solutions,
- To check this, all solutions were set to pH0,
- Measurements of 1/T₁ and 1/T₂ at different magnetic fields
- ⇒ All curves become similar ⇒ ⚠️ complexation.



Evolution with the field of 1/T₁ for (a) the original reduced solutions and (b) for the same solutions after the addition of HNO₃ to reach pH0.

5. Proof of concept with zerovalent aluminum



- Turbid suspension: ~~Spectroscopy~~,
- ⇒ NMR is the solution,
- In a single tube with 350 µl.
- Possible with zerovalent iron.
- Kinetics of the reduction of K₂Cr₂O₇ by zerovalent aluminum in the pH2 buffer, followed by T₂ relaxometry.

6. Perspectives

- Same experiments with other ions (iron, manganese, copper...)⁵,
- Study of the influence of magnetic compounds in the reaction mixture.

References

- Gossuin, Y. et al. Magn Reson Chem. 2023;61:284–295.
- Akpor, O.B. Adv. Biosci. Bioeng. 2014;2:37.
- Sharma, S.K. Heavy Metals in Water, Royal Society of Chemistry, London.
- Schlüter, A. et al, Z. Anal. Chem. 1973;266:177–186.
- Schlüter, A. et al, Analytica Chimica Acta. 1978;97:93–110.

Funding from FNRS-F.R.S. (CDR J.0093.22, CDR J.0025.15) and UMONS