Following chromium (IV) reduction by low resolution nuclear magnetic resonance relaxometry

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The measurement of the longitudinal and transverse relaxation rates is used to monitor the reduction, with hydrogen peroxide, of diamagnetic Cr^{6+} ions into paramagnetic Cr^{3+} ions in aqueous solution

1. Chromium in water – properties of chromium (VI) and (III)

- The presence of chromium in water is a major environmental and health concern[1],
- Chromium is released by stainless steel production, tannery and electroplating industries,
- Chromium (VI) is highly toxic when compared to chromium (III) => remediation by reduction[2-5]
- **Chromium (VI)** has full electronic orbitals → **non magnetic** → **no influence on water relaxation**
- **Chromium (III)** has three 3d electrons → **paramagnetic** → **shorten** water protons T_1 **and** T_2[6]
- The reduction of chromium (VI) to (III) in aqueous solution = decrease of T_1 and T_2

2. Conventional method to study the reduction of chromium (VI)

- Cr^{6+} concentration [Cr^{6+}] is often measured by the so-called "carbazide test",
- UV-Visible spectroscopy after addition of diphenylcarbazide to the solution[7],
- Really sensitive: limit of detection of 0.002 mg/ml, and linearity up to 2 mg/ml,
- Not suited for higher concentrations and restricted to clear solutions,

⇒ not always possible with wastewater or complex matrixes like muds,

⇒ Filtration needed, also when performing reduction with solid powders.

4. Monitoring of chromium reduction with relaxometry

- As expected, $1/T_1$ and $1/T_2$ increase because of the reduction (Fig.2),
- Linear decrease of $1/T_1$ and $1/T_2$ with the actual [Cr^{6+}] measured by direct spectroscopy (Fig. 3) → proportionality of $1/T_1$ and $1/T_2$ with [Cr^{3+}]

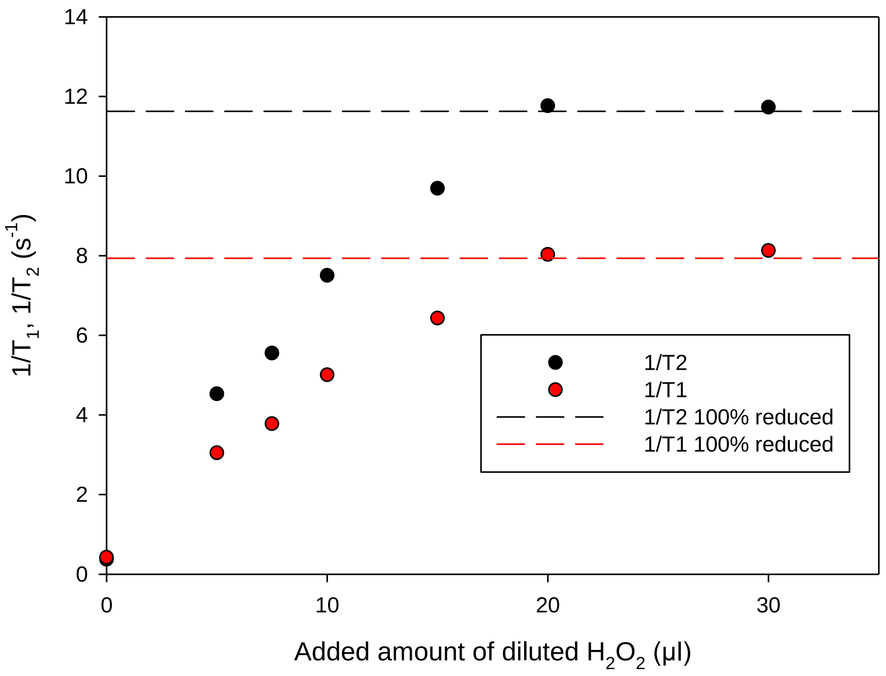

Figure 2: *evolution of T_1 and T_2 of a 1.5 mM Cr^{6+} solution after the addition of different amounts of 18 x diluted H_2O_2 at pH 1.7, 20°C and 0.47 T*

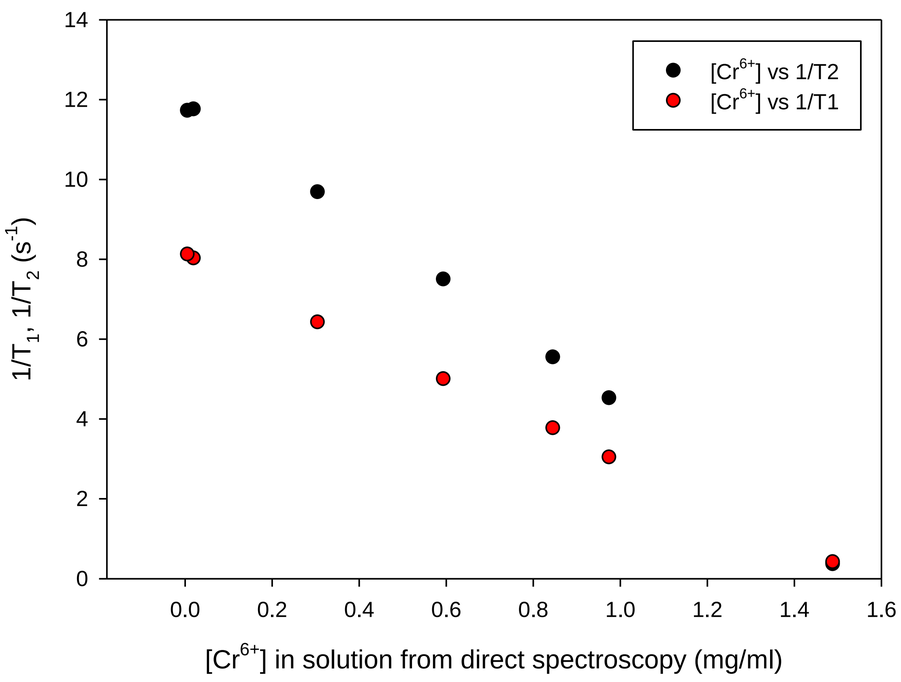

Figure 3: *correlation between the relaxation rates and the [Cr^{6+}] concentration measured by direct spectroscopy, at pH 1.7, 20°C and 0.47 T*

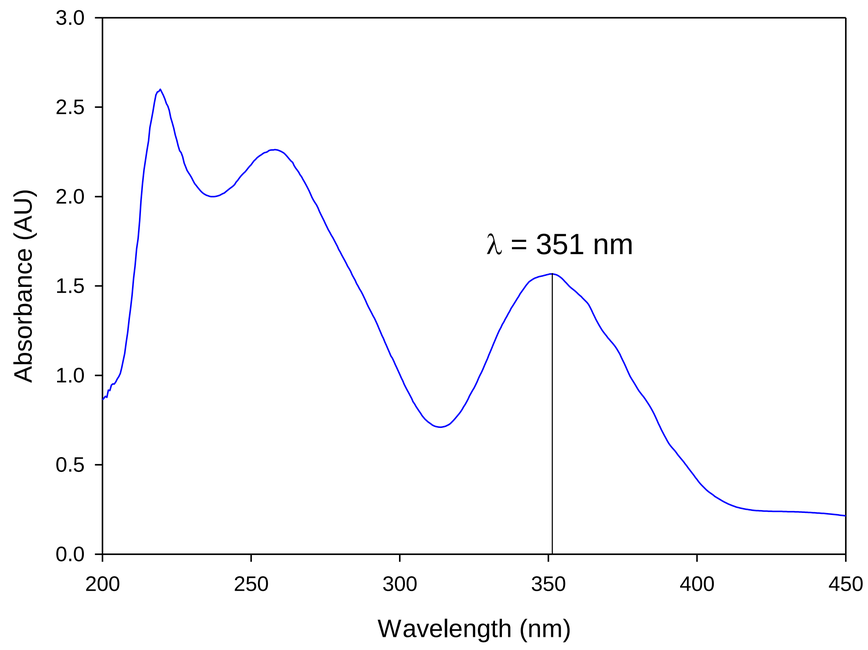

Figure 1: *typical direct absorption spectrum of a partially reduced 1.5 mM Cr^{6+} solution at pH 3. The absorbance at 351 nm was used for the determination of [Cr^{6+}]*

3. Material and Methods

- Reduction of 3 ml of 1.5 mM $K_2Cr_2O_7$ solution with diluted H_2O_2,
- After 72 h, measurement of T_1 and T_2 at 20 MHz,
- Independent measurement of remaining Cr^{6+} by direct UV-Visible spectroscopy (Fig. 1) without carbazide, as described previously[8],
- Study of the influence of pH, T and magnetic field on the relaxation of completely reduced Cr^{6+} solutions.

5. Relaxation properties of fully reduced Cr^{6+} solution

- Complete reduction of a 1.5 mM [Cr6+] solution,
- obtained using a higher concentration of H_2O_2 and confirmed by direct spectroscopy,
- Helps to find the best experimental conditions for the follow up of the reduction.

Figure 4 shows:

- T_2 more sensitive than T_1,
- High fields are better as $1/T_2$ increases,
- Important effect of temperature on the relaxation,
- Effect of pH on relaxation (not shown)

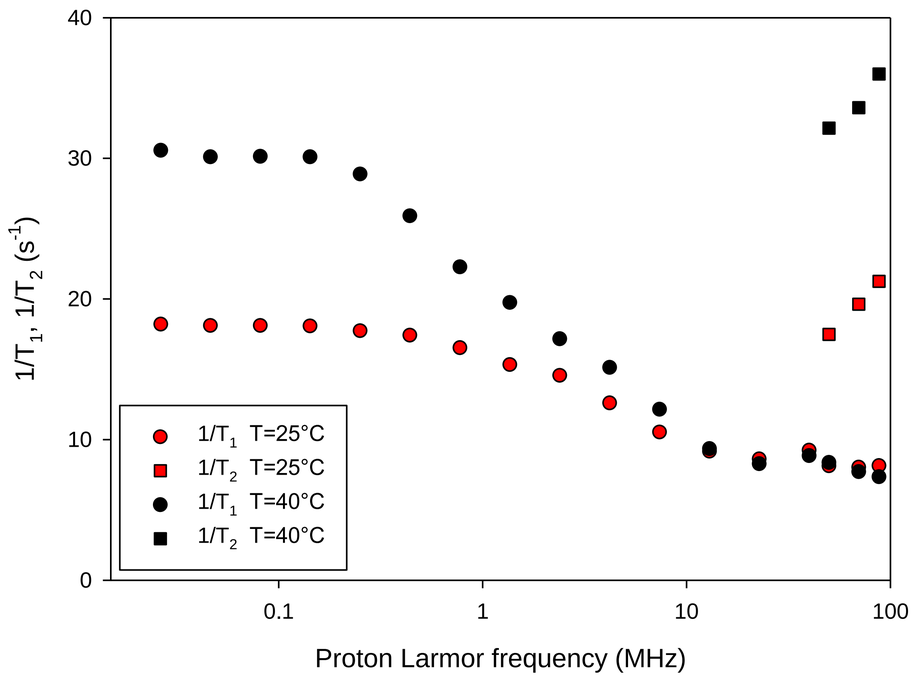

Figure 4: evolution with the field of the relaxation rates of a totally reduced 1.5 mM Cr^{6+} solution at pH 1.7

5. Perspectives

- Study of the reduction kinetics "live" in a single NMR tube,
- Follow-up of the reduction of Cr^{6+} by zerovalent aluminium,
- Follow-up of the reduction of Cr^{6+} by Fe^{2+} ions.

References

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