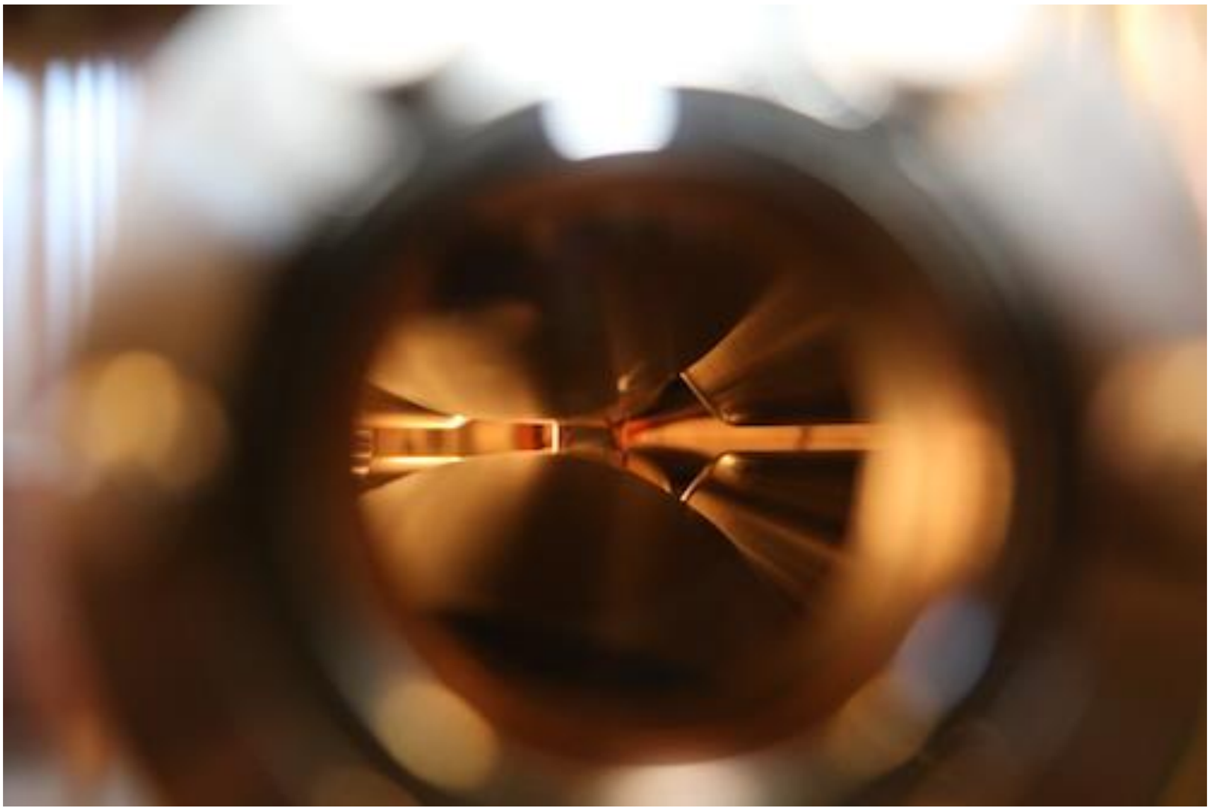
MAX-lab Activity Report 2013



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Local structure of Cr(III) in strongly alkaline aqueous solutions studied with XAS and UV-Visible spectroscopy

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Chromium(III) in low concentrations is an important trace element for humans, however, it can cause dermatitis, kidney and liver failure in higher dose. As chromium is an important compound of different kind of alloys and it is widely used in industrial procedures like leather tanning, tons of chromium contaminated waste produced per year. A common method to decrease the chromium(III) concentration is to precipitate it in alkaline media as $Cr(OH)_3$, which has very low solubility. Even it would be necessary, only a dozen of papers available about the speciation of chromium(III) above $pH = 13$ and there are some discrepancies within them [1].

According to some of the authors the dominating species is $[Cr(OH)_4]^-$ in strongly alkaline solutions while the others describe oligomer formation analogously with the slightly acidic media [2]. One of our aims was to resolve the contradictions about the alkaline speciation by the help of UV-Visible and X-ray absorption spectroscopy. In order to do it, the EXAFS spectrum of solutions containing 0.5 M chromium(III)-perchlorate and 8 M sodium hydroxide were taken. The solutions were aged for various times up to one month.

The measurements were carried out on the K-edge of the chromium (5989 eV) at MAX-lab, beamline I811. The data collection was performed in fluorescence mode. Higher order harmonics were reduced by detuning the second monochromator to 40% of the maximum intensity. The samples were placed in Teflon spacers of 0.2 mm thickness with Kapton tape windows. The collected data was treated by the EXAFSPAK program package.

The freshly prepared and the one week aged solutions were clear green and transparent, while the more aged ones were more viscous and some precipitate appeared in them. On the contrary all EXAFS spectra and their Fourier transform were the same, regardless the age of the solutions, as it is seen on Figure 1. This fact indicates two possibilities: the oligomerization takes place within minutes, or there is no oligomerization and the above mentioned changes of the solution in time have to be explained differently. By taking the UV-Visible spectrum of solutions containing 0.002 – 0.4 M chromium(III) in 8 M sodium hydroxide right after mixing it was proven that the second option is much more likely, as the normalized spectrum of these solutions matches each other perfectly, and this spectrum unequivocally belongs to the $[Cr(OH)_4]^-$ complex.

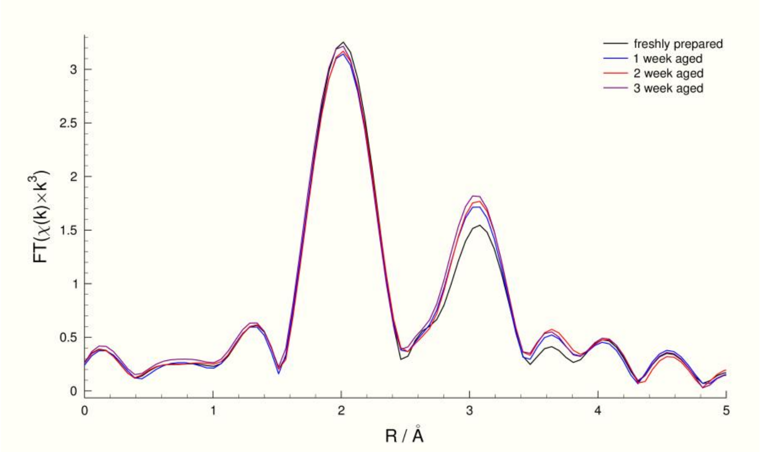

Figure 1. The Fourier transform of the EXAFS spectrum of 0.5 M Cr(III) and 8 M NaOH containing solutions aged for varying time.

The measured and fitted spectrum of the sample aged for one week are seen on Figure 2. The model described with three different Cr – O interatomic distances. The first coordination sphere consists of six Cr – O interatomic distance at 1.99 Å with σ^2=0.00154 Å^2. The second, wide peak of the pseudo-radial distribution function can be described with two distances at 2.93 Å and 3.29 Å, both with coordination number 8 and with Debye – Waller factors 0.00189 and 0.01208 Å^2, respectively (F=17.85%). This can be considered as the second hydration sphere of $[Cr(OH)_4]^-$ complex. Any attempt to describe the second peak by Cr – Cr interatomic distances (i. e., by oligomers) failed to provide better result, in accordance of UV-Vis measurements.

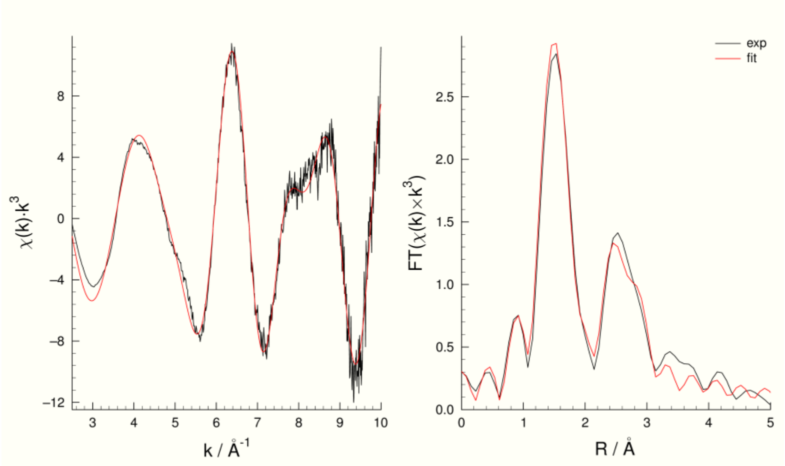

Figure 2. The EXAFS spectra and the Fouririer transform of it for the 1 week aged sample. Black: experimental spectra, red: fitted spectra.

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[2] N. Torapava, A. Radkevich, D. Davydov, A. Titov, I. Persson, Inorg Chem. (2009) 10383.