

X-RAY ABSORPTION SPECTROSCOPY STUDY OF PLATINUM CHLORIDE COMPLEX IONS IN AQUEOUS SOLUTIONS

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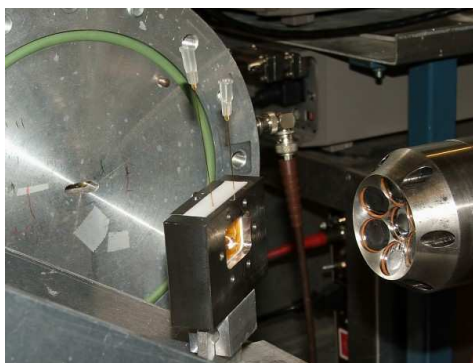


Figure 1. Sample holder for liquids mounted at the beamline X1 in the standard experimental set-up for absorption and fluorescence mode. Behind the sample holder the second ionisation chamber is visible, on the right side – 7 pixel fluorescence detector.

The investigations of noble metals chloride ions (*e.g.* Au, Pt or Ag) in the aqueous solutions are interesting due to the different reaction types involved (*e.g.* substitution, redox, complex) as well as due to the possibility for the synthesis of many valuable products. However, the reaction processes are not fully understood yet. Additionally, the standard experiments techniques, which have been used to investigate such reaction (*e.g.* spectrophotometry UV-Vis), in many cases are not able to detect the progress of the reaction as well as the change in the reactant structure. The example is the redox reaction of *e.g.* Pt, which can not be investigated by spectrophotometry, due to the precipitation of metal nanoparticles. Thus, the combination of X-ray absorption spectroscopy (XAS), in absorption and fluorescence detection, appears to be a suitable tool to investigate mechanism of the reaction.

In this paper we present first results of novel experiments at platinum chloride complex ions in aqueous solution under different pH conditions. Experiments have been performed at the beamline X1 at HASYLAB/DESY, Hamburg. The standard absorption setup together with 7 pixel fluorescence detector has been used. A special stopped-flow sample holder for liquids has

been constructed. The sample holder is presented in Fig. 1 together with the experimental set-up.

First, the experiment on $7.63 \times 10^{-3} \text{ M H}_2\text{PtCl}_6$ in aqueous solutions ($\text{pH} \approx 2.5$) has been performed in order to check that the sample is not influenced by the irradiation with X-rays. The repeated scans have shown that the Pt:L₃ edge position and shape, as well as the nearest neighbors' peak position and intensity do not change. The experiments have also shown no qualitative difference between EXAFS and QEXAFS (Quick EXAFS) spectra in the absorption mode. Thus, the QEXAFS could be exploited with the benefit of relatively short measurement time.

Next, experiments on $7.63 \times 10^{-3} \text{ M H}_2\text{PtCl}_6$ in aqueous solution with different pH have been performed. Results for pH of 2.5, 5 and 12 show the unchanged position and intensity of the nearest neighbors' peak. The effect could be studied in more details in the experiment on $7.63 \times 10^{-3} \text{ M H}_2\text{PtCl}_6 + 1 \text{ M NaOH}$ ($\text{pH} = 14$), where a decrease of the intensity of the nearest neighbors' peak is observed after few hours experiment, Fig. 2. We conclude that the hydrolysis of Pt is very slow and the reaction progresses during several hours.

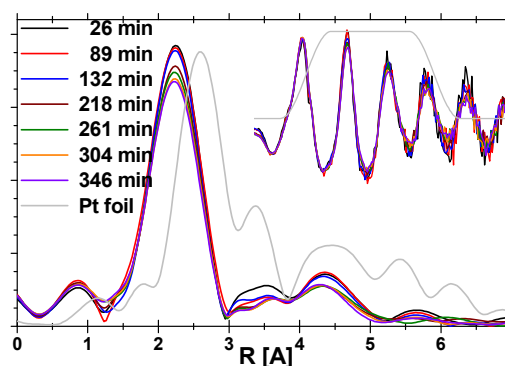


Figure 2. The Fourier transforms of the Pt:L₃ EXAFS functions for different time of hydrolysis of $7.63 \times 10^{-3} \text{ M H}_2\text{PtCl}_6 + 1 \text{ M NaOH}$.