	Experiment title:	**Experiment number**:
	Hydrolysis of X-Ser peptide promoted by molybdate(VI) oxyanions	26-01-932
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Report:

Hydrolysis of the dipeptide Gly-Ser was examined in the presence of sodium molybdate, $[MoO_4]^{2-}$ by means of ^{1}H and ^{13}C NMR spectroscopy. The ^{1}H NMR spectra show a gradual intensity decrease of the Gly-Ser resonances and the appearance of a resonance that is attributed to free glycine, indicating that the cleavage of the peptide bond in Gly-Ser occurred. The pH dependence of k_{obs} was measured in order to identify the catalytically active molybdate species. Comparison of the rate profile with the concentration profile of polyoxomolybdates suggests that the monomeric molybdate, $[MoO_4]^{2-}$ is the hydrolytically active species.The coordination mode of Gly-Ser was studied by examining the effect of $[MoO_4]^{2-}$ on the ^{1}H and ^{13}C NMR spectra of Gly-Ser. In addition EXAFS measurements were performed to get more insight in de binding of the dipeptide to $[MoO_4]^{2-}$. Understanding the coordination of peptides to the molybdenum species active in the hydrolysis of X-Ser peptide bond allows the identification of the mechanism for this novel reaction. In addition the gained knowledge will allow us to understand the mechanism of peptide and protein hydrolysis promoted by other oxyanions which we are currently investigating.

Solutions containing $[MoO_4]^{2-}$ at different concentration and pH values were prepared and used to optimize the experimental EXAFS setup for the Mo K-edge. At pH 7.0, the use of 2 mM $[MoO_4]^{2-}$ resulted in an optimal S/N and the molybdate was present in its hydrolytically active form. Once the setup was calibrated and optimized, these solutions were used as blank measurements to study the molybdate species distribution as a function of pH and concentration. For each sample 3 runs were measured. This resulted in an approximate measurement time of 3 h for each sample. These measurements were important since they allowed us to identify the species present in the absence of the dipeptide and will be compared to the ones containing the dipeptide at the same concentrations and pH conditions. Solutions containing 2 mM sodium molybdate in the presence of Gly-Ser, Ser-Gly, or His-Ser were prepared as a function of pH. In addition different concentration ratios ranging from a 1:2 to a 1:20 ratio of molybdate to the dipeptides were measured. The spectra recorded for the 1:20 sample of His-Ser are significantly different from those of the 1:0 sample at the same pH. The EXAFS spectra recorded for the intermediate concentration ratios can be interpreted as a combination of the spectra observed for the 1:0 and 1:20 sample.