

Electrochemical characterization of humic substance redox properties

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Humic substances act as electron donors/acceptors and as electron shuttles. As such, humics are of key importance in many biogeochemical cycles and in pollutant dynamics. The objective of this work was to characterize the major redox-properties of humics using an electrochemical approach.

First, we developed a new chronoamperometric method using a carbon working electrode (negligible background current from H^+ reduction) to transfer known amounts of redox equivalents (RE) to model humic acids (HA). Reduction for 20h at $E=-0.6V$ (SHE) and pH 7 resulted in RE transfer that increased in the order Suwannee River HA ($510 \mu\text{equiv g}^{-1}$), Pahokee Peat HA ($930 \mu\text{equiv g}^{-1}$), Leonardite HA (LHA) ($1030 \mu\text{equiv g}^{-1}$) and Elliot Soil HA ($1190 \mu\text{equiv g}^{-1}$), and correlated with values reported in [1]. Second, we employed mediated cathodic and anodic chrono-amperometric detection to quantify the RE in a set of LHA samples pre-reduced to different redox states. Detection of the RE in LHA was quantitative (95% of transferred RE were detected), irrespective of the degree of LHA pre-reduction. This method quantifies RE directly by current measurement at very low detection limits. Third, we studied the re-oxidation kinetics of reduced LHA ($1050 \mu\text{equiv g}^{-1}$) by excess O_2 at pH 7. The re-oxidation kinetics were strongly biphasic: fast initial transfer of 40% of the RE to O_2 in less than 1 min was followed by slow LHA re-oxidation over 5d, at which 12% of RE still remained in LHA. Biphasic kinetics are taken to reflect the variability in the reactivity of the redox-active moieties in HA. Fourth, we coupled the reduction of LHA to H^+ titration (Fig. 1). The ratio e^-/H^+ transferred during reduction decreased from 1.00 at pH 7 to 0.86 at pH 9, 0.75 at pH 10 (not shown), and 0.38 at pH 11. This strongly supports that quinone-type moieties dominated the redox-properties of LHA, as hydroquinones deprotonate successively at $pH > 8-9$.

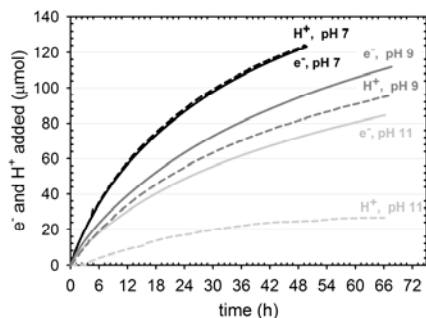


Figure 1: Electrochemical reduction of 0.15g Leonardite humic acid coupled to H^+ -titration at pH 7, 9, and 11.

[1] Ratasuk & Nanny (2007) *ES&T* **41**, 7844.

Noble gas temperatures from speleothems

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Speleothems have proven to be excellent paleoclimate archives, providing accurately dated high-resolution stable isotope and trace element records. However, the interpretation of such data in terms of past temperatures is difficult. Noble gases dissolved in microscopic water inclusions in speleothems have the potential to provide direct paleotemperature information, in analogy to noble gas paleothermometry in groundwater. While the extraction and precise measurement of noble gas concentrations from speleothem samples of about 1 g are feasible, the main difficulty of the method arises from the often large amounts of air included in the samples. Apparently only few speleothems provide naturally low air to water ratios suitable for noble gas temperature (NGT) determination. However, stepwise extraction procedures can reduce this ratio and thereby increase the number of speleothems accessible by the method. In addition to temperature, the water content of speleothems appears to provide useful information on paleohumidity.

Several speleothems from Bunker Cave in Northwest-Germany provided the first reasonably precise NGTs. Combined data from two stalagmites yield a temperature record encompassing several relatively warm phases during the past ~130 kyr. A large temperature increase of about 9°C is found at the transition into the Eemian Interglacial, which appears to have been significantly warmer than the Holocene. The early Eemian warming correlates well with high resolution stable isotope data, highlighting the potential of the method to calibrate the stable isotope paleothermometer. NGTs during the Holocene show no significant variation within the uncertainties of about ± 1 to 2°C. Variations of the water content in this cave as well as a cave from southern Chile are correlated to established humidity indicators such as stable isotopes and Mg/Ca ratios, suggesting that wet phases and high drip rates lead to comparatively high water contents in the stalagmites.