# Complexation of Molybdenum(VI) with Humic Substances from Greek Leonardite: Spectroscopic Insights and Implications for Soil Bioavailability

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**Humic substances (HS), derived from organic matter degradation in terrestrial and aquatic systems, have major impact on a myriad of physical, chemical and biological phenomena including nutrient cycling, metal complexation, and soil fertility.**

**Mo is an essential micronutrient regulating nitrogen fixation and assimilation. Despite Mo's pivotal role, its solubility and bioavailability in soils remain limited, often leading to deficiencies in plants.**

**Understanding Mo–HS interactions is therefore crucial for developing sustainable strategies to improve nutrient availability.**

**HS from Greek leonardite of the Megalopolis basin**

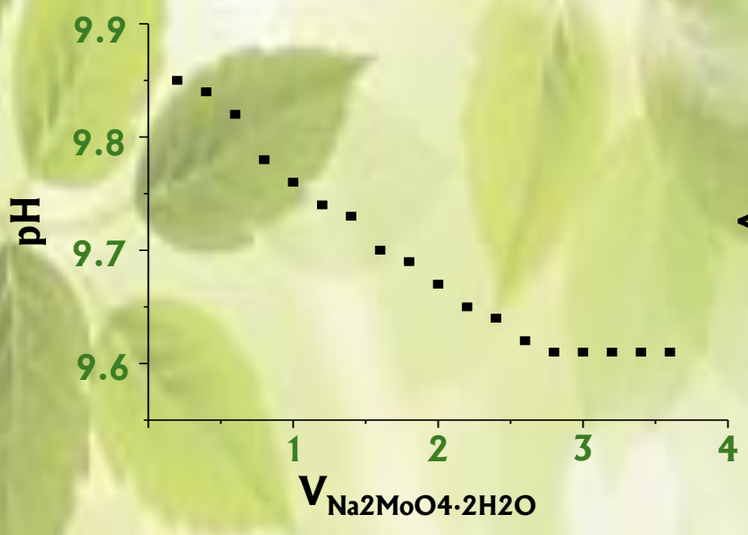
Absorbance ratios of HS

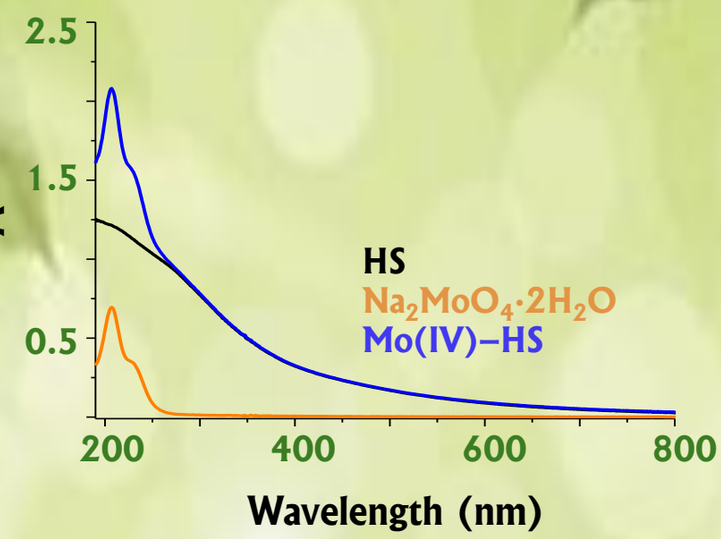
| $A_{250}/A_{365}$ | $A_{465}/A_{665}$ | $A_{254}/A_{203}$ | $A_{280}/A_{350}$ | $A_{265}/A_{465}$ | $A_{254}/A_{436}$ | $A_{210}/A_{254}$ |
|---|---|---|---|---|---|---|
| 2.385 | 3.559 | 0.838 | 1.781 | 4.595 | 4.037 | 1.179 |

**Macromolecular fractions polycondensedwith C/O ratios and low acidity**

## Complexation

**The formation of Mo(VI)-HS complexes during addition of Mo(VI) ions to HS solutions proceeded via proton-release reactions**

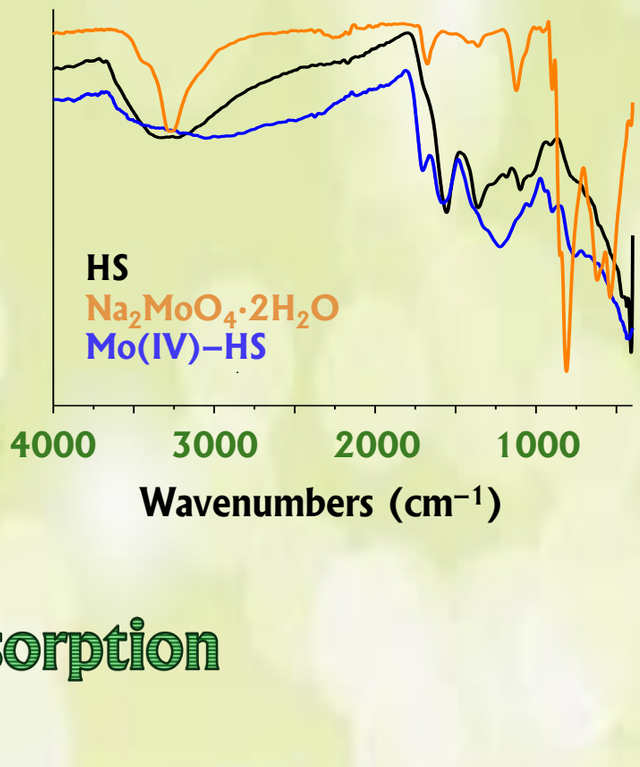


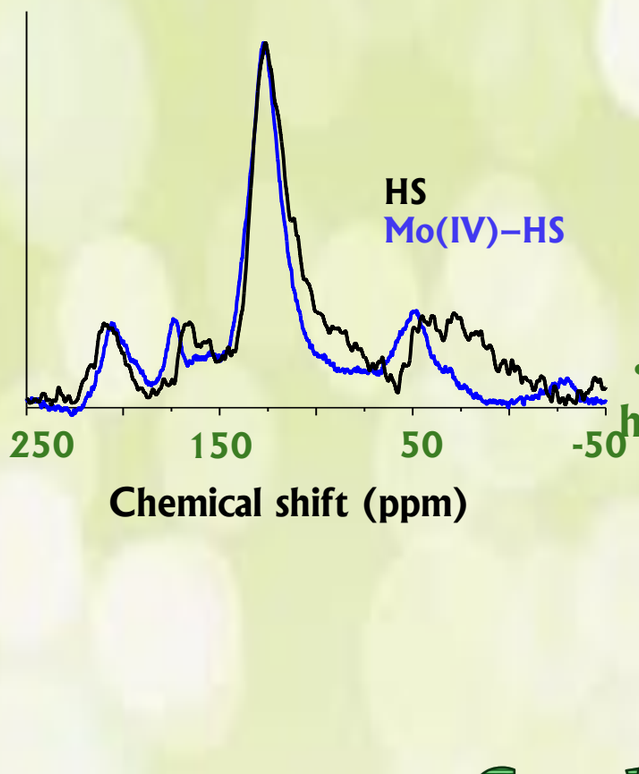




**UV-Vis spectra indicated alterations in the relative intensities of the Mo(VI) doublet peaks below 280 nm due to Mo(VI)-HS interactions**

## Characterization

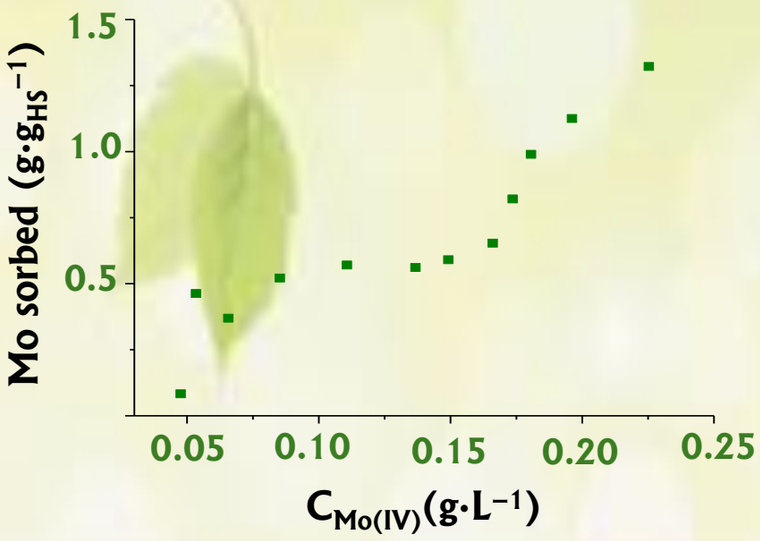
**FTIR**
**Mo(VI)-HS complexes:**
- **bear coordinated water (enhancement of the 3100 to 3700-$cm^{-1}$ peak)**
- **involve –OH groups (intensity reduction near 3280 $cm^{-1}$)**
- **involve –COOH groups (changes at 1560- and 1360-$cm^{-1}$)**




**13C CP/MAS NMR**
- **peak broadening due to reduced mobility and increased anisotropy**
- **upfield shift of alkyls, aromatics and carboxyls**
- **participation of carboxyl, hydroxyl and ketonic groups in Mo(VI)-HS association**

## Adsorption




- **Type II adsorption isotherm**
- **1.3 g Mo / g HS (maximum adsorption) useful to treat soil Mo deficiencies**
- **High adsorption is useful to slow-release applications**

## Conclusions

- **HS effectively complex Mo(VI)**
- **Mo-HS complexation enhances Mo solubility and bioavailability in soils**
- **The agronomic potential of humic-rich materials, such as leonardite, as natural Mo carriers for improving crop nutrition is highlighted.**
- **A broader understanding of HS-mediated trace element dynamics and their role in sustainable agriculture.**

**References**
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