FT-IR Investigation of Glucoheptonate Chelation

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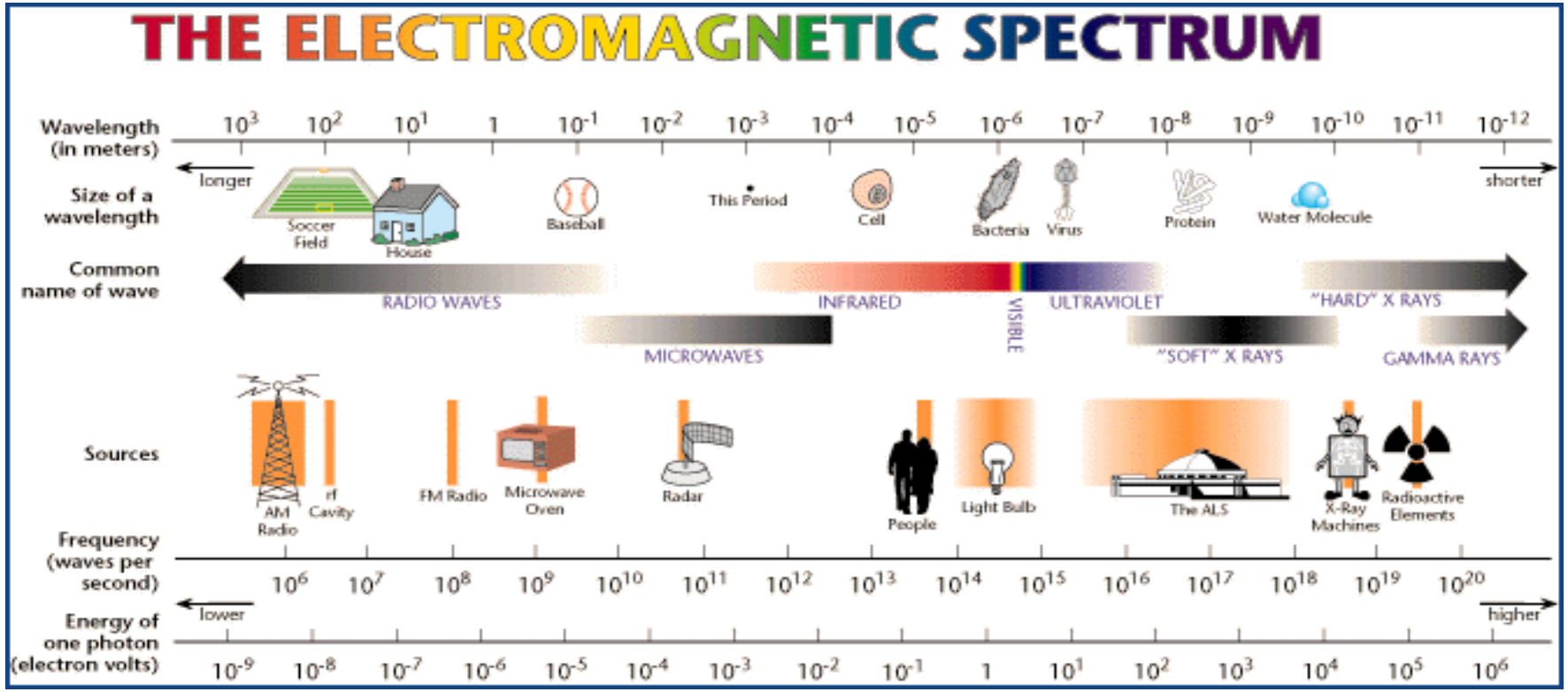
LIGHT

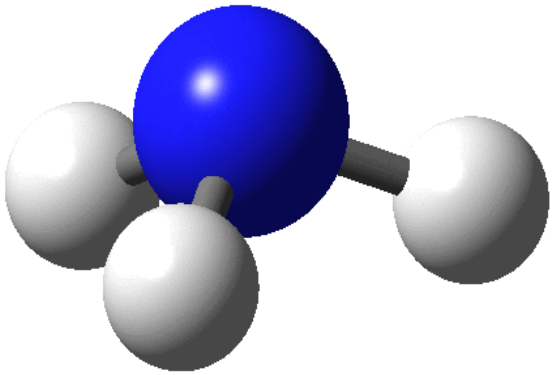
Classification of Electromagnetic Radiation



Light rays are electromagnetic waves: they can be define by their frequency or their wavelength (λ).

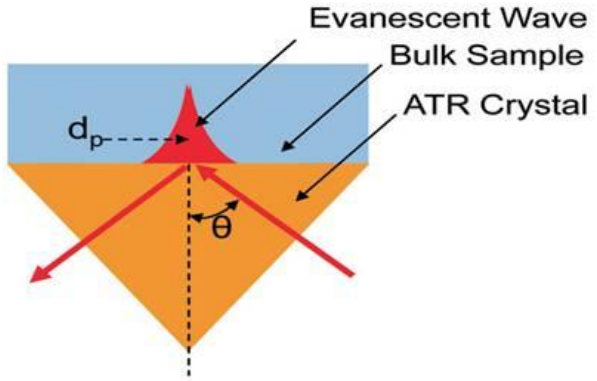
Infrared Spectroscopy: Overview

- Chemical bonds are like springs. They vibrate (bend, stretch, etc).
- Infrared light can be absorbed by these vibrations, increasing their energy levels.
- Frequency is characteristic of the bonds involved
- polarity, geometry, symmetry, selection rules
- Spectral range typically 4000 to 450 cm^{-1} .
- (2500 nm to 22200 nm)
- Molecular fingerprint



Attenuated Total Reflection - ATR

- When radiation is totally reflected internally at an interface with a material of lower refractive index the electric field penetrates a short distance beyond the interface. This field, called an *evanescent wave*, can be absorbed by a sample on the surface.
- The electric field decreases away from the surface and the *penetration depth* (d_p) is defined as the distance at which it falls to 1/e of its value at the surface.
- Penetration depth depends on the angle of incidence (θ) and the refractive indices of crystal and sample and is also proportional to the wavelength (1).
- For a diamond ATR element, the penetration depth at 1000 cm^{-1} is typically 1–2 μm.
- Because of the wavelength dependence, the penetration depth increases by a factor of 10 between 4000 and 400 cm^{-1}



[1] F.M. Mirabella, *Internal Reflection Spectroscopy* (Marcel Dekker, New York, 1993).

Perkin Elmer Spectrum 2 with UATR

- Single reflection diamond ATR crystal, epoxy bonded into 316 Stainless Steel
- Minimal Sample prep, just evaporate a drop of solution onto crystal
- Easy clean up
- A few minutes per sample

Studies:

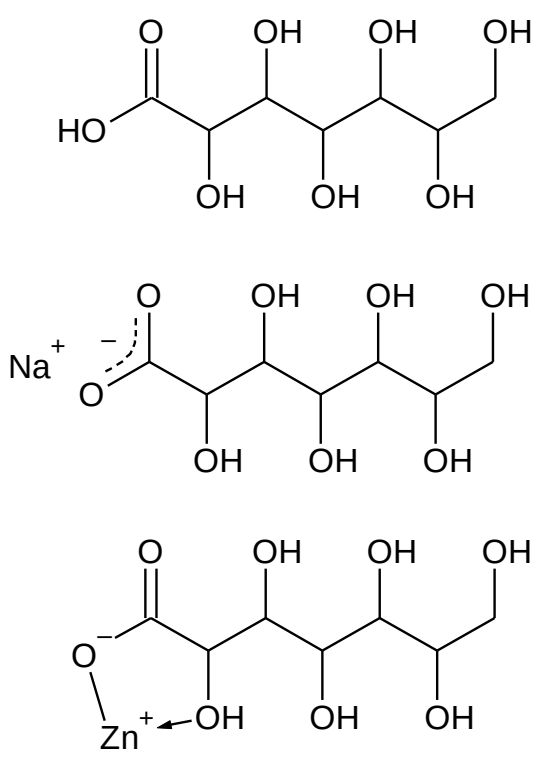
- Prepare solutions of metal cations and sodium glucoheptonate.
- Zn, Mn, Fe and Cu
- Sodium Glucoheptonate is not chelated[2] while Zinc Glucoheptonate, Zinc Gluconate[3,4] and Manganese Gluconate[5] are.
- Compare FT-IR ATR spectra of glucoheptonates of Mn, Cu and Fe with zinc glucoheptonates.

2. 2. Y.J Park, B.H Lee, Acta Cryst. C57, 12 (2001).
3. H.A. Tajmir-Riahi, *Can. J. Chem*, **67,** 651 (1988)
4. G.M. Escandar, M.G. Sierra, J.M.S. Peregrin, G. Labadie, M. Santoro, A. Frutos, L.F. Sala, *Polyhedron*, **13**, 909 (1994).
5. T. Lis, *Acta Cryst.*, **B35**, 1699 (1969).

Experimental

- Prepare series of aqueous solutions with constant sodium glucoheptonate concentration while varying cation content.
- Cations derived from metal chlorides. Byproduct, sodium chloride, does not have covalent bonds and is infrared transparent.
- Solution is placed on ATR crystal (after background of clean crystal obtained) and dry air used to evaporate water leaving behind metal glucoheptonate.
- Spectra recorded in absorbance and normalized with respect to glucoheptonate content.
- Grams/AI (Thermo) used for analysis

What Kind of Changes to be seen?



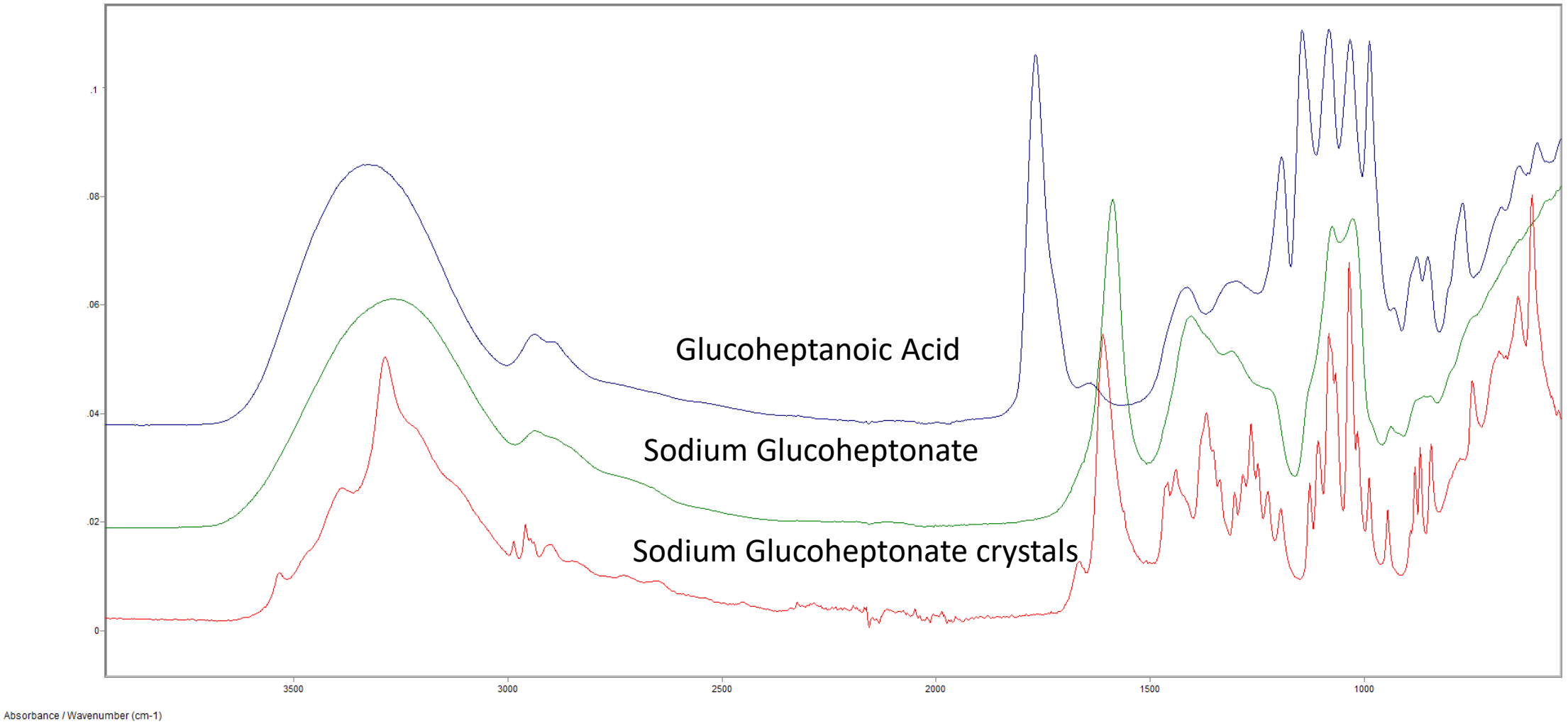
- Reacting glucoheptanoic acid to the sodium salt: Conversion of carboxylic acid to carboxylate ion, chelation not present

Chelation with metal cation:

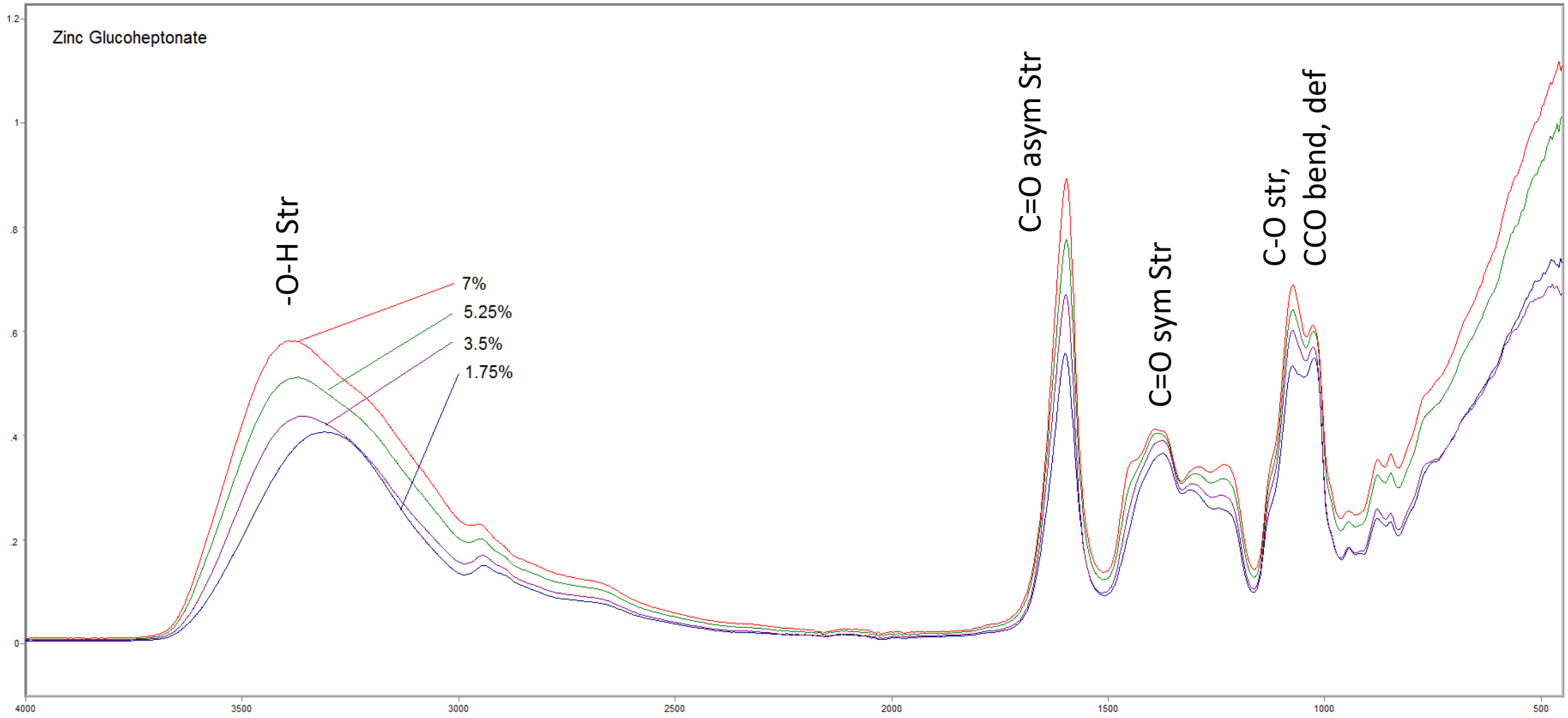
- Change in frequency and intensity of carboxylate ion[6]
- Change in C-O bending / deformation modes due to change in bond angle (5 membered ring)[7,8]
- Changes in O-H stretching frequency and Intensity[7,8]

6. H.A. Tajmir-Raihi, *Carbohydr. Res.*, **122**, 241(1983)
7. E. Wiercigroch, E. Szafraniec, K. Czamara, M. Z. Pacia, K. Majzner, K. Kochan, A. Kaczor, M. Baranska, Kamilla Malek, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 185, 317 (2017)
8. A.P. Kilimov, M.A. Svechnikova, V.I. Shevchenko, V.V. Smirnov, F.V. Kvasnyuk-Mudri, S.B. Zotov, Chemistry of Heterocyclic Compounds, 3, 647 (1967).

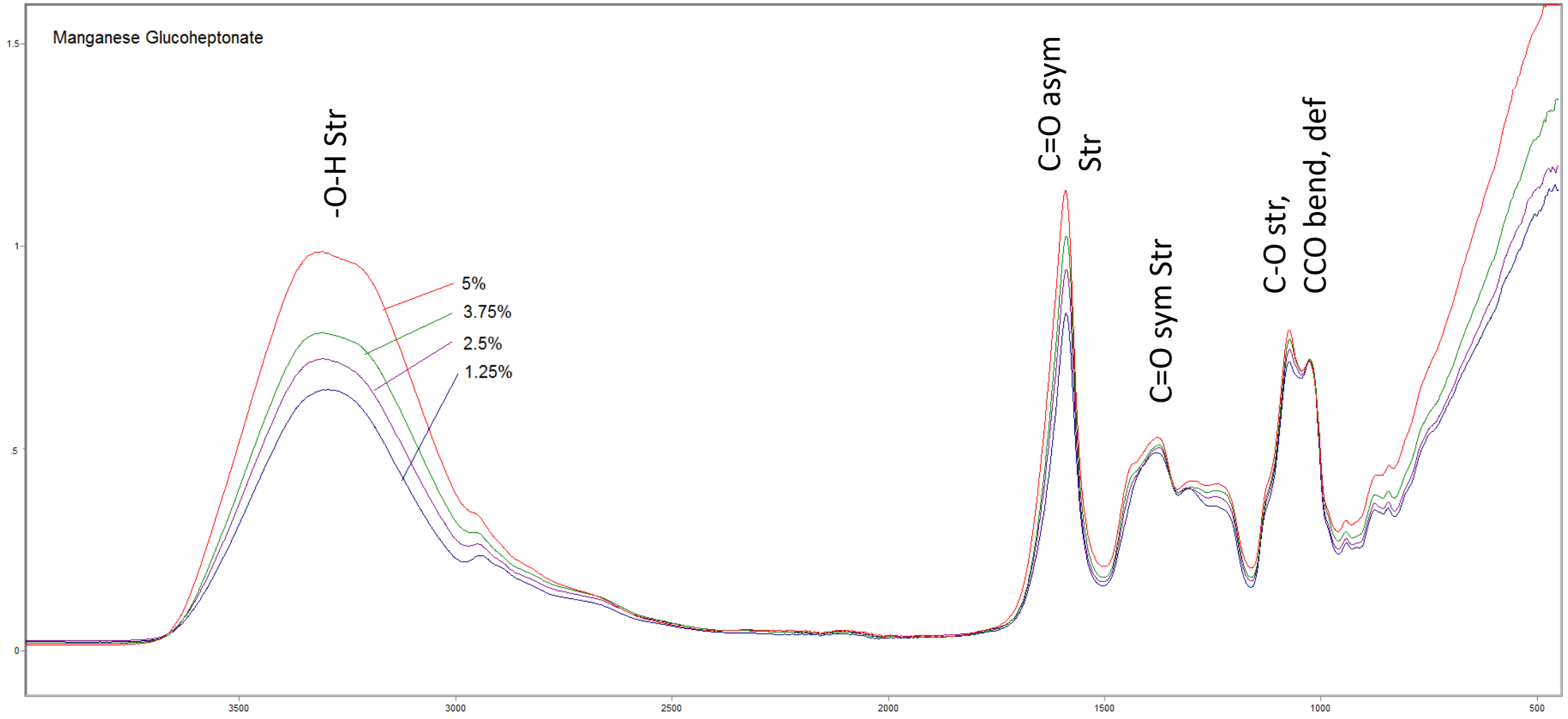
What Kind of Changes to be seen?



Control: Zinc Glucoheptonate

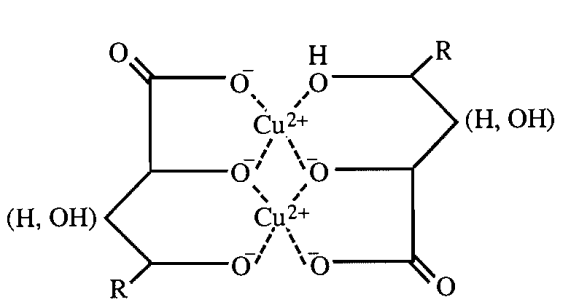


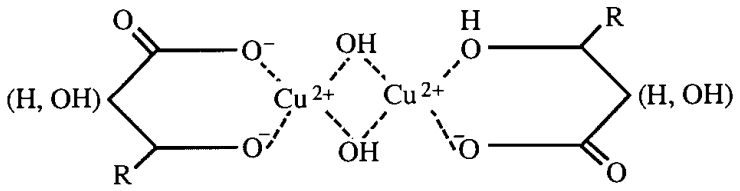
Manganese Glucoheptonate

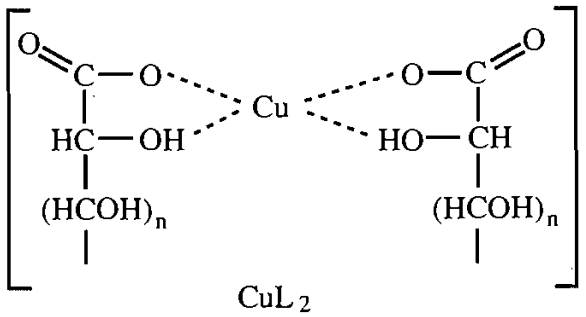


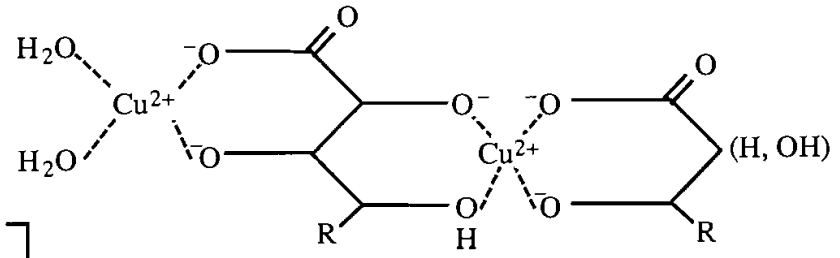
Copper Glucoheptonate

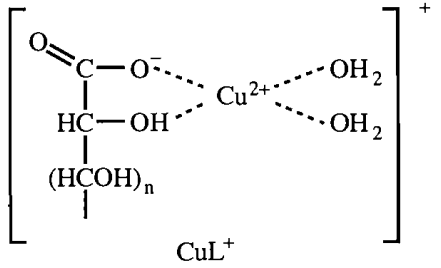
Complex mixture of multiple types of chelated species.





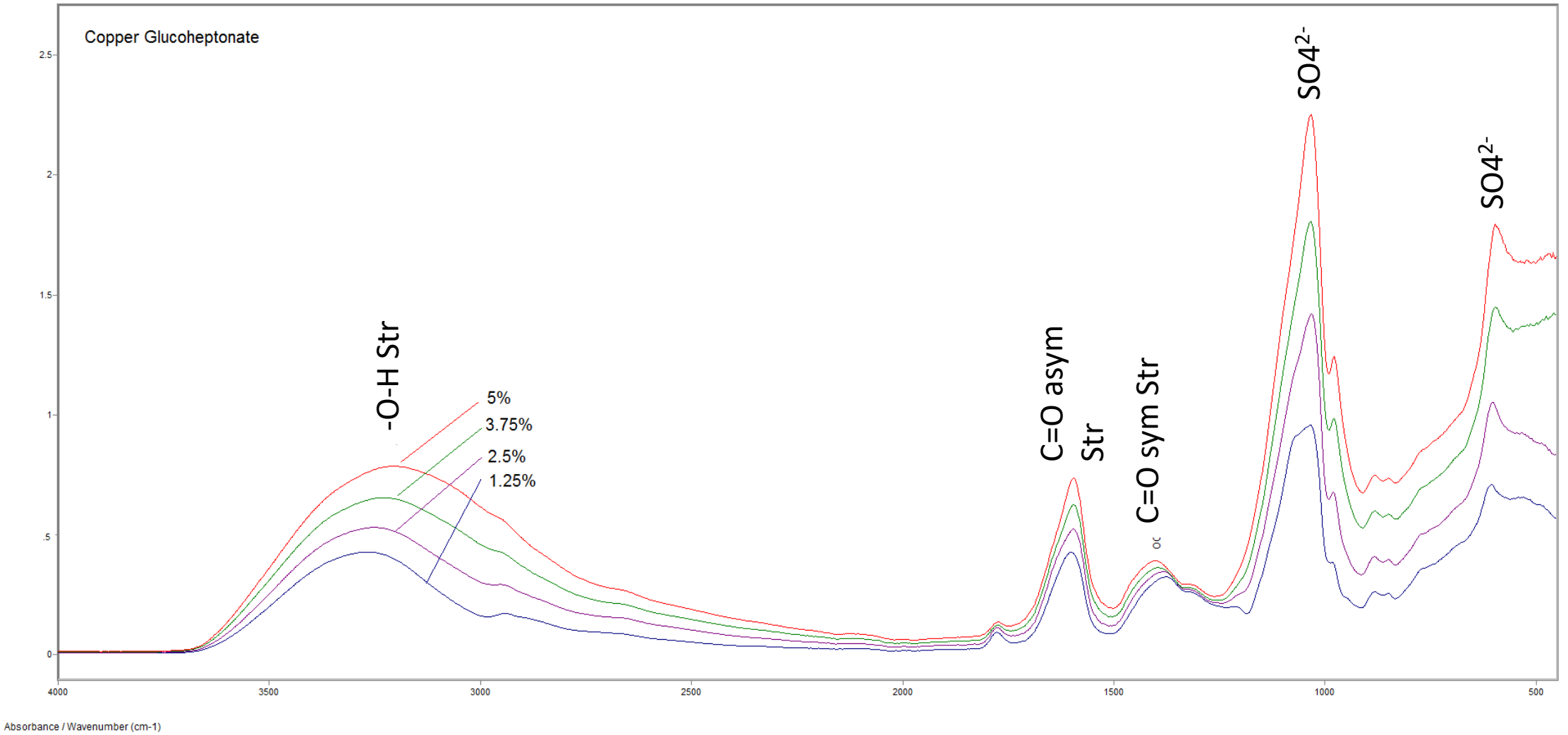




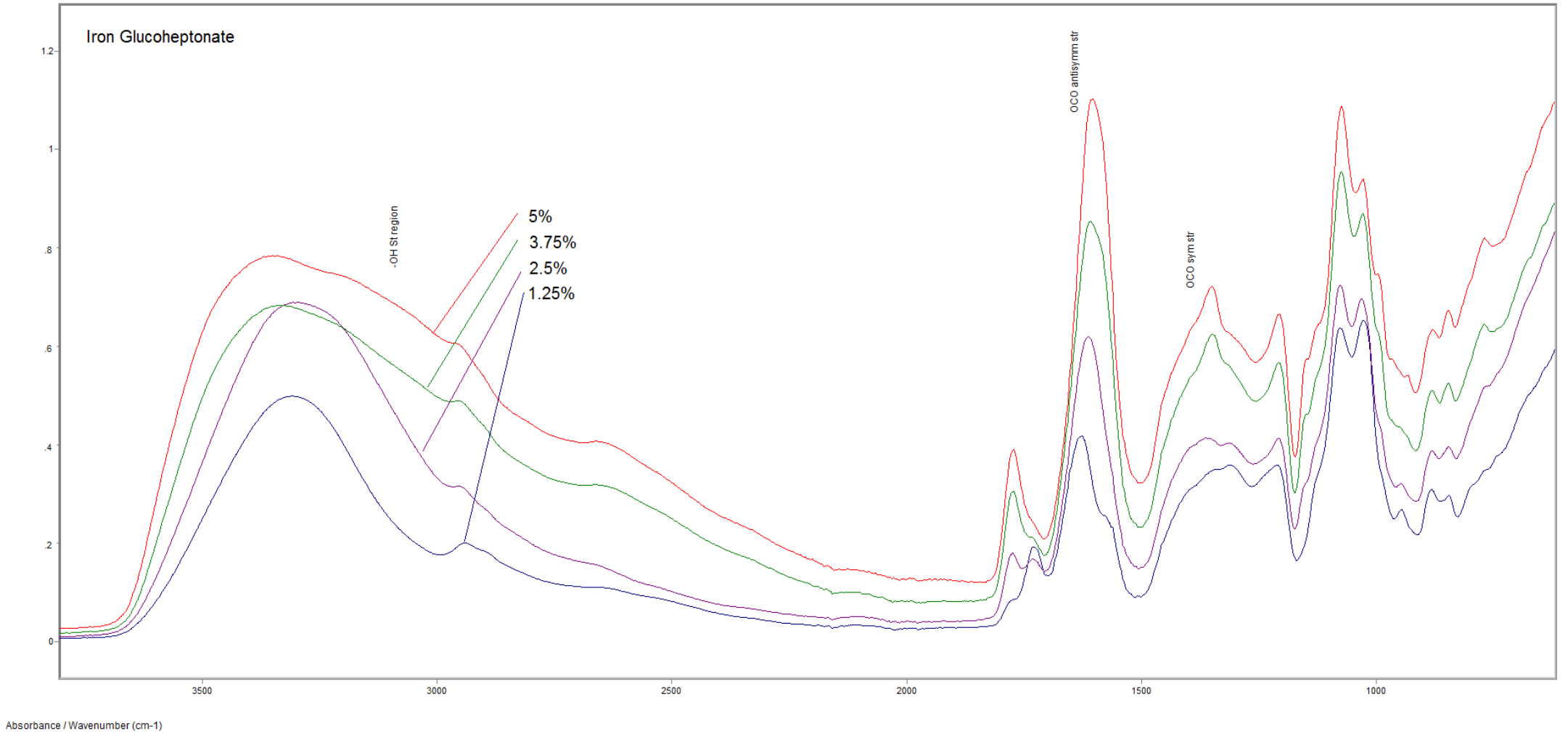


9. G.M. Escandar, L.F. Sala., “Complexes of Cu(II) with D-aldonic and D-alduronic acids in aqueous solution” *Can. J Chem*., **70**, 2053 (1992)

Copper Glucoheptonate



Iron Glucoheptonate



Summary

- ATR effective tool for investigating changes related to metal glucoheptonate chelation.
- Zinc Glucoheptonate model compound
- Manganese Glucoheptonate follows similar spectral changes
- Copper complex mixture of chelated forms
- Iron similar to copper

Limitations and Opportunities for More Work

- Work is primarily qualitative.
- Compare sodium glucoheptonate with metals to reaction with glucoheptanoic acid?
- Chemical environment effects on spectra?

Acknowledgements

- Ray Thompson, Perkin Elmer
- Kolin Alfonso

Questions?