AAPFCO - Summer 2020 Meeting – Chelation of Transition Metals by FT-IR – Revised 7/22/2020

Eric Johnson, Chemical Dynamics, Inc, Plant City FL

The use of FT-IR ATR spectroscopy was previously reported to AAPFCO for the February 2020 Lab Services meeting. This report extends the initial studies of chelation of sodium glucoheptonates with Manganese, Iron, Zinc and Copper divalent metal ions.

In the previous study reported, it was observed that their were changes associated with the carboxylate bands that are associated with binding to a metal cation and there were changes associated with bands in the C-O stretch and deformation region around 1000 to 1100 cm-1 for zinc and manganese glucoheptonates. Copper and iron glucoheptonates presented more challenging spectra but were last minute preparations of suspect materials.

In the continuation of this study, copper and iron were prepared from fresh metal chlorides. Moreover, manganese and zinc gluconates were also studied since these have been previously reported in the literature. Published X-Ray crystallography has shown sodium glucoheptonate is not chelated [1] while manganese gluconate is chelated [2]. The manganese gluconate is studied here as a spectral reference to indicate changes associated with chelation of gluconates and glucoheptonates.

X-Ray and spectrographic features of zinc gluconate and zinc glucoheptonate are very similar to the previously mention manganese gluconate indicating similar molecular structures [3,4]. Similar structures are expected to have similar spectrographic features.

In this study, the ratio of carbohydrate and metal cation is varied. The metal cations are derived only from metal chlorides and their solutions are evaporated under ambient conditions onto the ATR element of an infrared spectrometer. This represents the form a dried residue would have upon application.

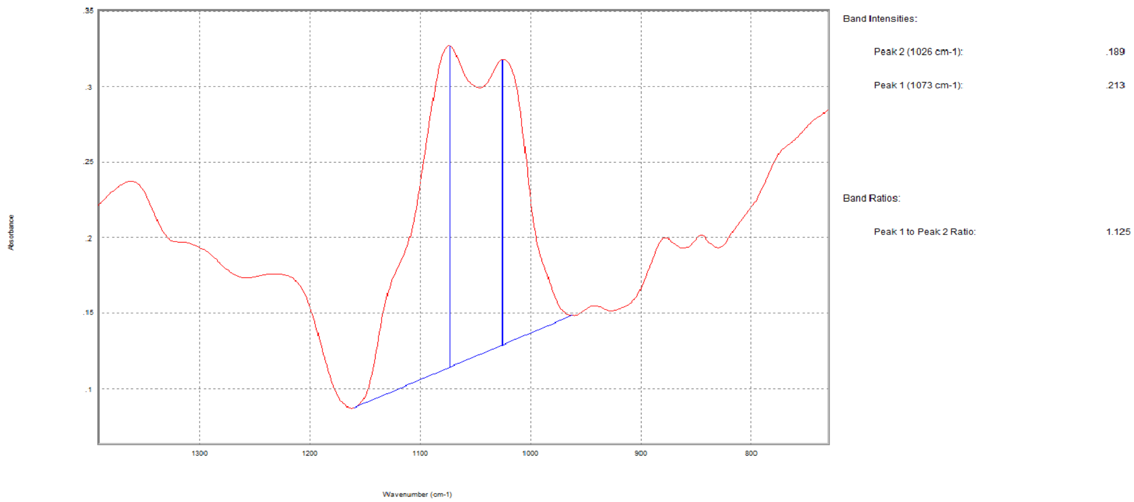
As previously described, this work investigates changes in the carbohydrate that are expected to be associated with changes from a non-chelated form to a chelated form. Under chelation, the oxygen of the hydroxyl group immediately adjacent to the carboxylate group is expected to attach to the metal cation and form a five membered ring. Such changes result in changes in the bond angle around the hydroxyl oxygen, changes in the bond strength of the associated -O-H bond and the associated transition dipole moments. Such changes should be apparent in the infrared spectra of these materials as the metal content of the mix increases relative to the carbohydrate content.

Manganese gluconate will be used as a reference compound since this is a known chelated material. Changes in the infrared spectra of the gluconate moiety will be reflective of changes relating to chelation as the manganese level increases.

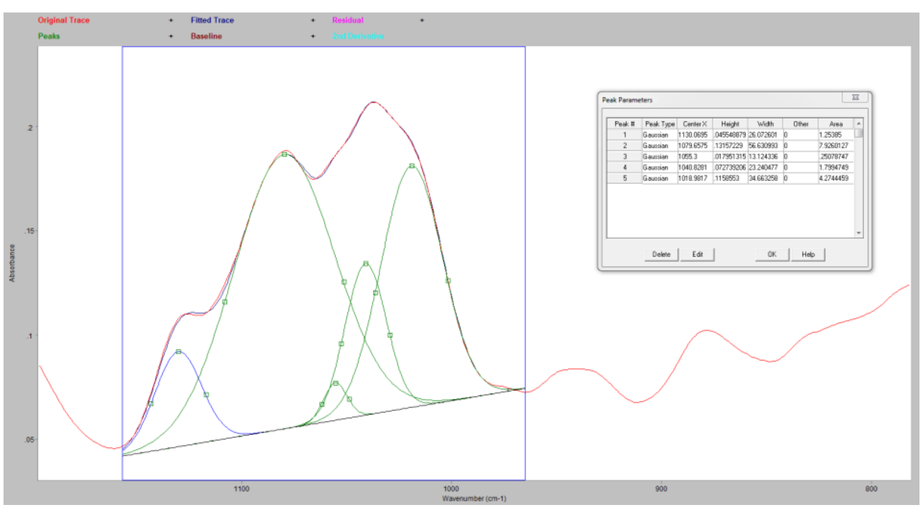
Experimental

The spectra were recorded using a Perkin-Elmer Spectrum 2 equipped with a UART accessory using a diamond ATR crystal element at 4 cm-1 resolution. Spectra were imported into Thermo Grams/AI spectral analysis software package for analysis. Solutions were prepared from metal chlorides and sodium glucoheptonate from Aldrich Chemical Company. Samples were solution cast onto the UATR element and evaporated under ambient conditions using a stream of dry air. Real time monitoring of the sample was done during the evaporation process until the spectrum of water was no longer visible. The byproduct of the chelation reaction is sodium chloride which is infrared transparent in the spectral regions of interest and does not spectrally interfere.

For the four glucoheptonates, the baseline fitted band ratio between the absorbances at 1073 to 1026 cm-1 were calculated. The figure blow shows one example of how the absorbancies were calculated for the 5% Copper (in solution) Glucoheptonate sample after air drying.



Similar ratios were calculated for zinc gluconate and manganese gluconate. These spectra were complicated by the significant presence of a band at 1040 cm-1 which is weaker in the glucoheptonates and had minimal interference. So rather than calculating simple band ratios at 2 wavenumbers, this spectral region was curve fitted. The example shown in the figure below is a screen shot of the fitting for 5% Manganese (in solution) Gluconate after air drying. The band ratios were calculated based on the band absorbancies at the center of the bands centered at 1080 and 1020 cm-1, which are the analogous bands seen in the glucoheptonates.



Results

For all samples studied, the rations for the bands between 1080 cm-1 and 1020 cm-1 increase with increasing cation content relative to the carbohydrate in question. The table below shows the increase in band ratio with increasing metal ion content relative to the carbohydrate.

<u>Observed Band Ratios:</u>

	Glucoheptonates			Gluconate			Glucoheptonate	Gluconate
% Metal*	Fe	Cu	Mn	Mn		% Metal*	Zn	Zn
0	0.995	0.995	0.995	1.116		0	0.995	1.116
1.25	1.016	1.013	1.028	1.136		1.75	1.005	1.122
2.5	1.090	1.034	1.095	1.168		3.5	1.109	1.156
3.75	1.128	1.070	1.150	1.198		5.25	1.154	1.231
5	1.248	1.125	1.222	1.217		7	1.248	1.313

* metal percentages are in solution. The quantity of carbohydrate was kept constant in all samples. A higher % metal means more metal relative to the carbohydrate.

Conclusion

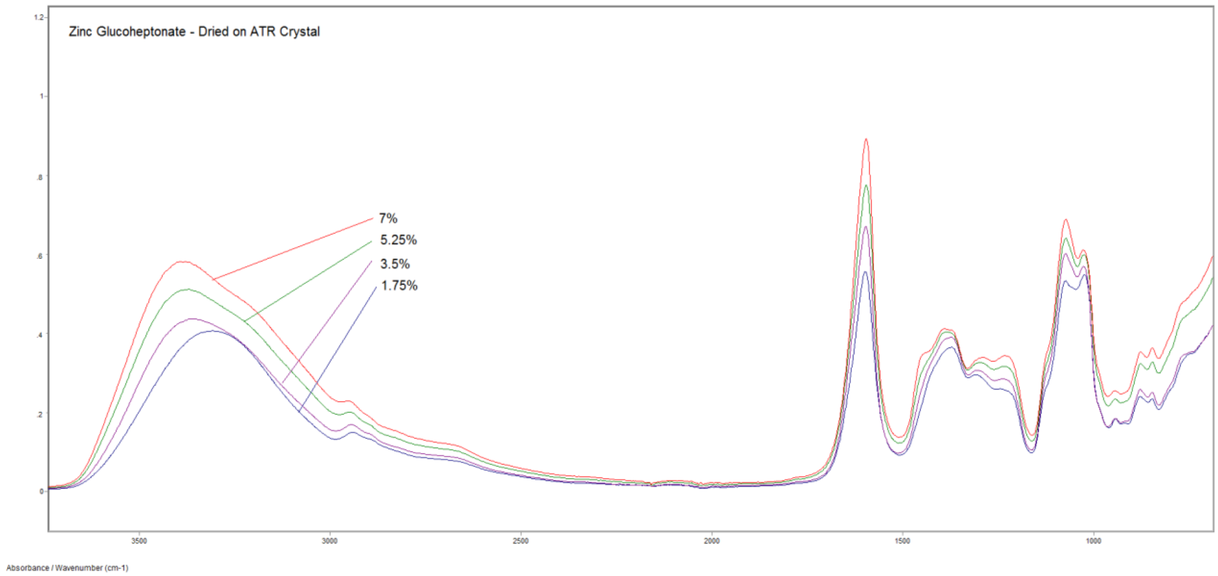
The increase in band ratio for manganese gluconate, the known chelated reference species, exists across all the metal/carbohydrates studied. The individual spectral overlays are appended to this study. This indicates the molecular structures of the metal glucoheptonates studied and zinc glucoheptonate directly parallel the molecular structure changes observed by vibrational spectroscopy in manganese gluconate, a known chelated material.

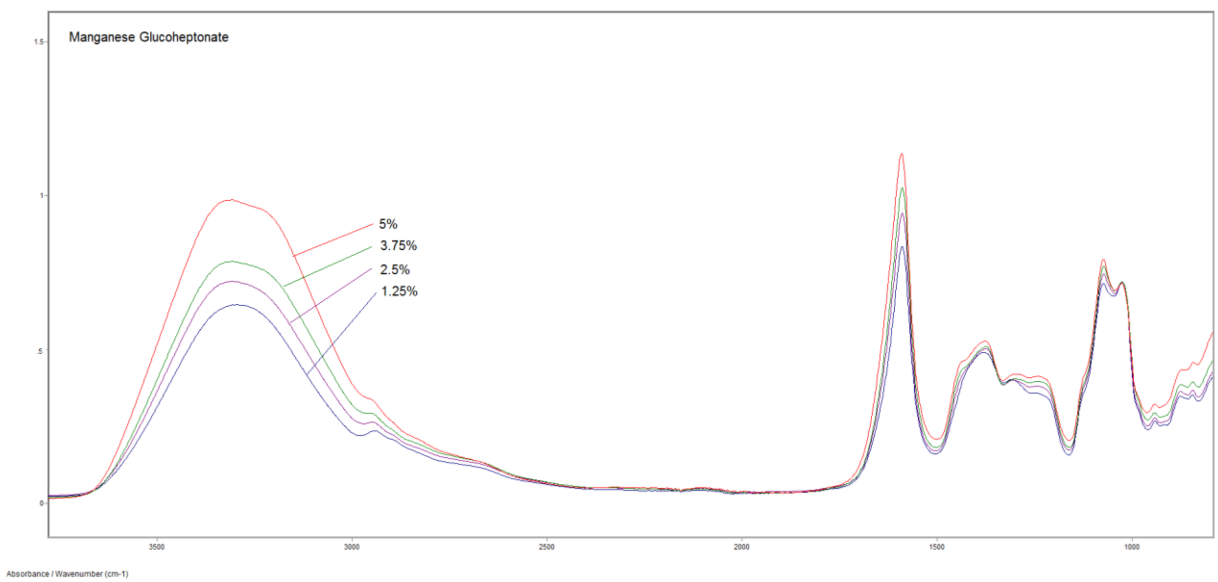
[1] Y.J Park, B.H Lee, Acta Cryst. C57, 12 (2001).

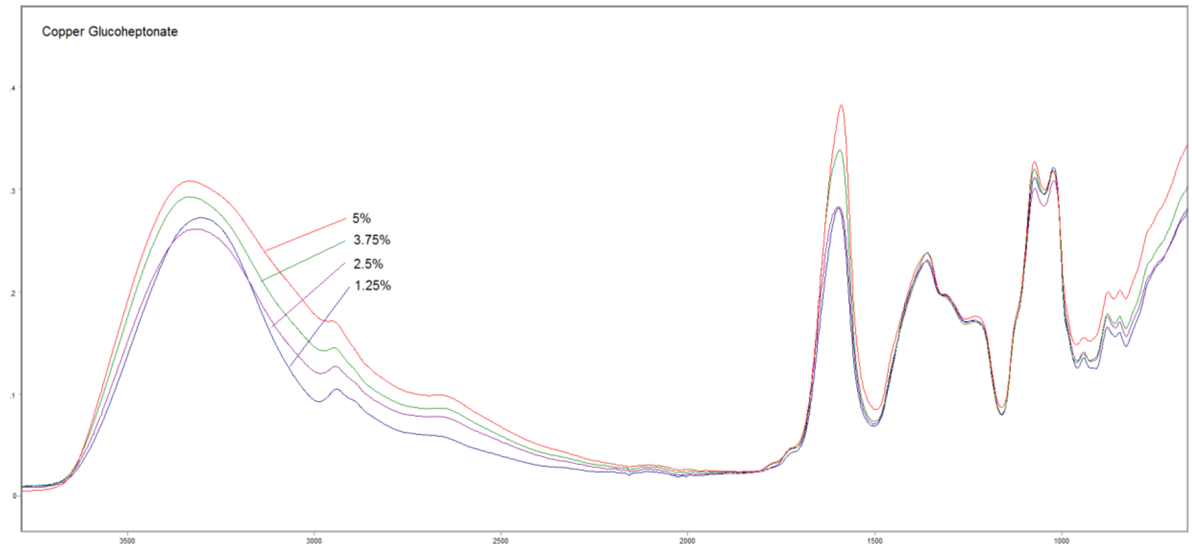
[2] T. Lis, Acta Cryst., B35, 1699 (1969)

[3] H.A. Tajmir-Riahi, Can. J. Chem, 67, 651 (1988)

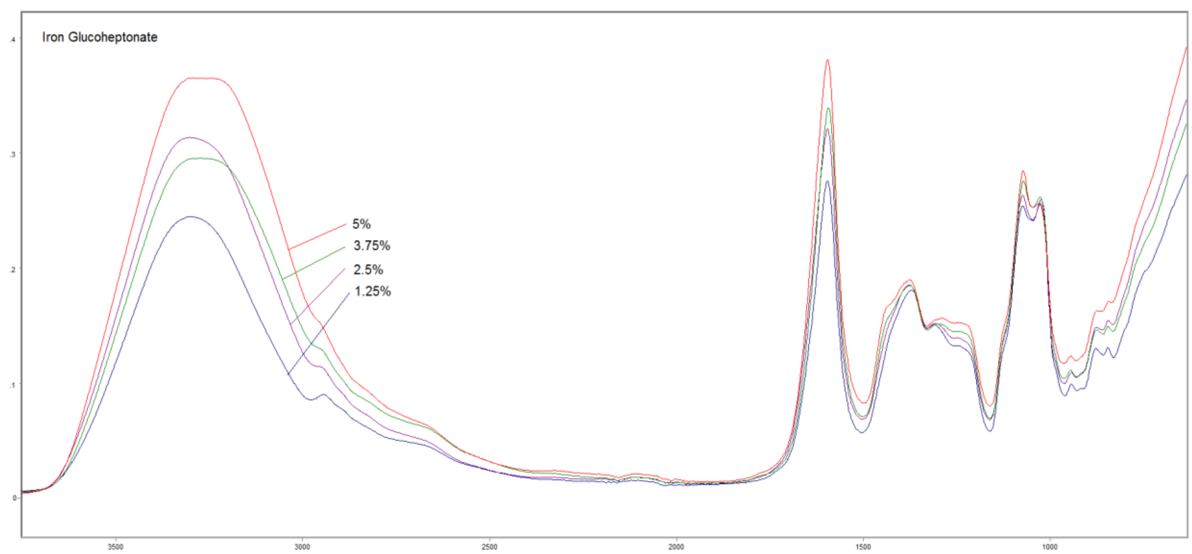
[4] G.M. Escandar, M.G. Sierra, J.M.S. Peregrin, G. Labadie, M. Santoro, A. Frutos, L.F. Sala, Polyhedron, 13, 909 (1994).


Zinc Glucoheptonate - Dried on ATR Crystal
7%
5.25%
3.5%
1.75%
Absorbance / Wavenumber (cm-1)

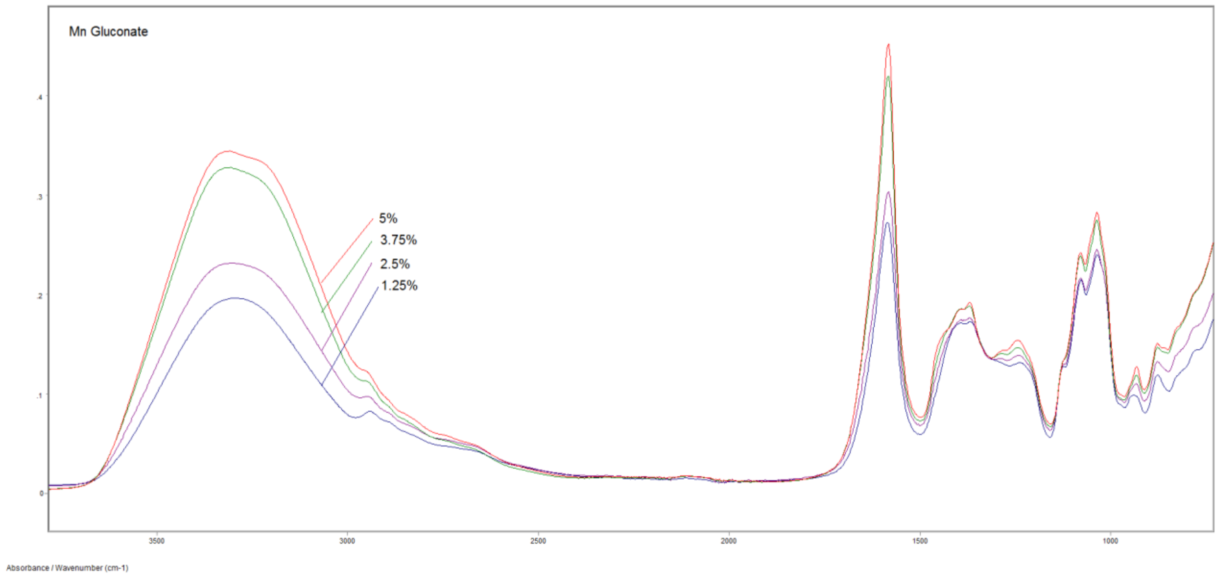

Manganese Glucoheptonate
5%
3.75%
2.5%
1.25%
Absorbance / Wavenumber (cm-1)

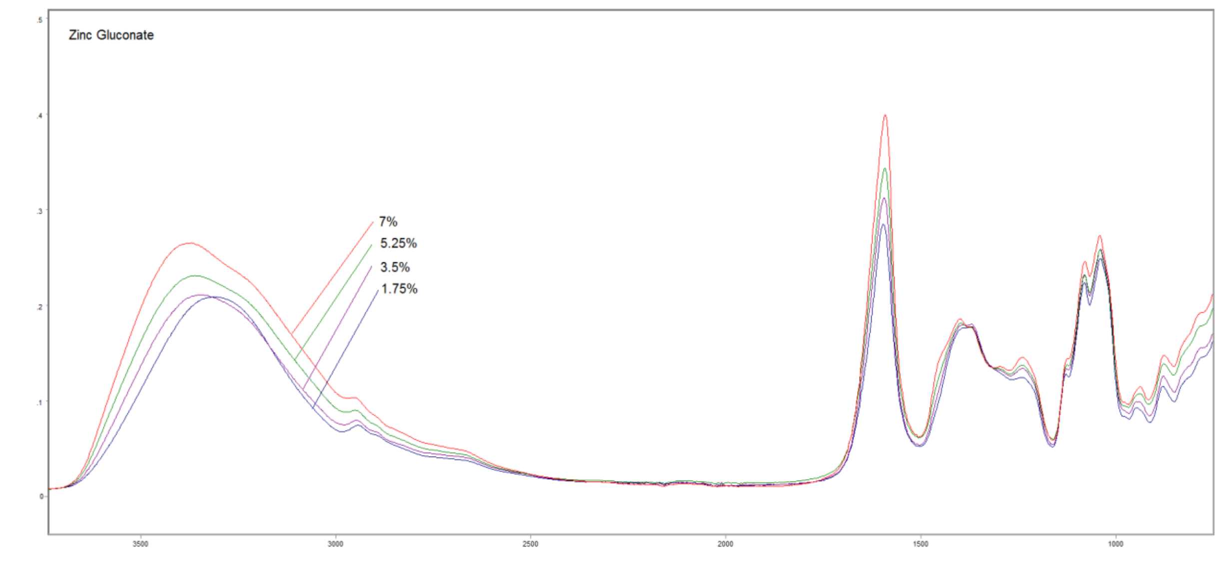


Absorbance / Wavenumber (cm-1)



Absorbance / Wavenumber (cm-1)


Mn Gluconate
5%
3.75%
2.5%
1.25%
.4
.3
.2
.1
0
3500
3000
2500
2000
1500
1000
Absorbance / Wavenumber (cm-1)


Zinc Gluconate
7%
5.25%
3.5%
1.75%
.5
.4
.3
.2
.1
0
3500
3000
2500
2000
1500
1000
Absorbance / Wavenumber (cm-1)