

# Challenges with Chelated &/or Complexed Minerals (Chelated and Soluble Methods of Analysis Used in FL)

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# Total, Soluble and Chelated Micronutrients

## Fertilizer Sample

- Total Iron = 6.5%
- Soluble Fe = 5.0%
- Chelated Iron = 3.0%

Derived from: Iron oxide, iron sulfate and iron EDTA



# Types of Sources

- Soluble Fe, Cu, Mn, Zn Micronutrients-
  - Sulfates, chlorides, nitrates, succrates
- Chelated Fe, Cu, Mn, Zn Micronutrients-
  - FeEDTA, CuEDTA, MnEDTA, ZnEDTA, FeHEDTA, FeDTPA, FeEDDHA, iron citrate, lignosulfonates



# Water Soluble Micronutrient Extractions

- Soluble Manganese

- Samples are extracted in pH 5 potassium hydrogen phthalate buffer solution (0.05M).
- In samples containing high phosphate ( $\%P_2O_5 \geq 10\%$ ) and the source is MAP, DAP or polyammonium phosphate, the soluble manganese can be precipitated as manganese ammonium phosphate. This is significant at pH above 5.2, especially if the extracts are allowed to sit overnight.
- Liquid samples containing ammonium polyphosphate must be extracted in 10% disodium EDTA solution due to the strong complexing characteristics of ammonium polyphosphate for manganese. The disodium EDTA extraction solution solubilizes the manganese because it has a stronger chelating affinity for manganese than the strongly complexing ammonium polyphosphate.



# Water Soluble Micronutrient Extractions

- Soluble Copper and Zinc
  - Samples are extracted in pH 6.0 buffer solution (0.24M 2,2 Bis(hydroxymethyl)-2,2',2''-nitrilotriethanol (C<sub>8</sub>H<sub>19</sub>NO<sub>5</sub>) and hydrochloric acid).
  - Liquid samples containing ammonium polyphosphate must be extracted in 10% disodium EDTA solution due to the strong complexing characteristics of ammonium polyphosphate for the micronutrient. The disodium EDTA extraction solution solubilizes the micronutrient because it has a stronger chelating affinity for the micronutrient than the strongly complexing ammonium polyphosphate.
- Soluble Iron
  - Samples are extracted in 1% sulfuric acid solution.



# Analysis Time Constraints

- Zinc Oxides are slightly soluble
  - Zinc sample must be analyzed within 1 hour of weighing into buffer solution.
  - The solubility of zinc oxides increases with time under these pH conditions.
- Soluble Manganese with  $P_2O_5$  10% or greater
  - Samples must be analyzed on the same day as the buffer extraction.
  - Manganese ammonium phosphate precipitates can form which is significant at a pH above 5.2 and the extract is allowed to sit overnight.
- Soluble Copper and Iron
  - Sample extracts may be allowed to sit overnight before analyzing.



# Chelated Micronutrient Extractions

- Chelated Fe, Cu, Mn, Zn are extracted with a sodium acetate buffer solution at an acidic pH range between 3 and 4.
- An acidic extraction solution is specified to compensate for the basic condition brought about when large amounts of dolomite or limestone are used as fillers.
- The acidic extraction prevents iron chelates from undergoing irreversible ligand exchange reactions with copper, manganese, zinc and other metal ions and forming of insoluble iron salts. Ferric (Fe<sup>+3</sup>) iron forms insoluble salts at pH >3 if no complexing agent is present.
- Filter and Analyze within 30 minutes.



# Chelated Micronutrient Extractions

- In samples containing non-chelated ferrous sulfates, the addition of the hypochlorite and ammonium phosphate reagents oxidizes ferrous iron to ferric iron which readily forms insoluble precipitates.
  - Reagents are only necessary when ferrous salts are present
  - Higher concentrations of sodium hypochlorite or longer reaction times may result in some loss of chelated iron.
- If soluble ferrous sulfate is present or results are excessively high (%found is 3X>% guarantee), weigh sample into buffer solution and add 15 ml of hypochlorite solution and 15 ml of diammonium phosphate solution to sample.
- Bring to volume with DI H<sub>2</sub>O and shake for 30 seconds. Allow samples to sit for 5-10 minutes, to ensure precipitation reaction goes to completion.





# Iron Chelate - Pure Material Extraction

- This extraction procedure is only appropriate for pure iron chelates (Reference AOAC 983.03)
- Sample is dissolved in DI water and allowed to settle.
- Sample is filtered and diluted and the pH is adjusted to 8.5 with 0.2 N sodium hydroxide to precipitate out any non-chelated iron as  $\text{Fe}(\text{OH})_3$
- If the pH drifts above 8.8, discard solution and repeat the sample preparation.
- Filter and collect filtrate, acidify with 2-3 drops HCl.
- Analyze within one hour using AA.



# Recent Challenges/Future Plans

- Soluble Copper and Soluble Zinc
  - Intermittent problems where soluble results are lower than total results when sulfate is the only source listed
- Future Work Planned
  - Evaluate sources and combinations of other sources in sample and possible effects on methodology
  - Move methods to ICP

Is anyone else working on Chelates or Solubles Methodology?



# Questions?



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