CONGRESO IBEROAMERICANO DE INVESTIGACIÓN EN CELULOSA Y PAPEL 2002
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# CHELATING AGENTS IN *Eucalyptus* KRAFT PULPS

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# I. PHOSPHONATES IN PULPING AND BROWN STOCK WASHING

# Introduction

- TCF vs. ECF
  - Environment
  - Strengh
  - Costs

- Hydroxyl radical (HO•), extremely reactive and indiscriminate.
- Generated by peroxide decomposition.
- Catalyzed by metallic ions present in pulps.

# Introduction

- Hydrogen peroxide is an intermediate in the stepwise reduction of $O_2$ in oxygen delignification.
- The hydroxyl radical can also be produced in this stage.

# Introduction

- Process loses selectivity, attacking the carbohydrates.
- Controlling organic peroxides formation and reaction will promote better brightness and physical properties of pulps.
- Since wood itself contains $Mn^{+2}$; $Fe^{+3}$ and $Cu^{+2}$, metal management in an early stage of pulp production or handling could be advantageous.

# Introduction

- A pretreatment of pulp in a Q separate stage is usually performed to eliminate heavy metals, and prevent peroxide decomposition.
- But chelating agents may be added at several points in a TCF sequence.

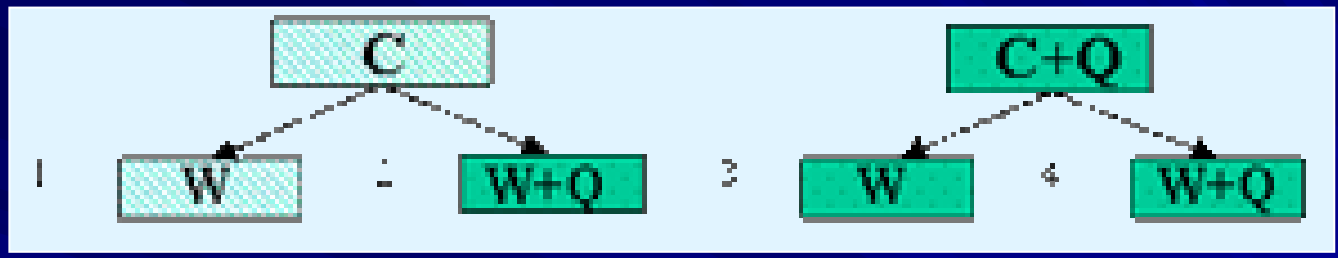
# Introduction

- An aspect to consider in chelating agent selection is pulp pH.
- An important cost reduction could be achieved if the intermediate acidification is eliminated.
- While EDTA requires acid conditions, most phosphonates function well in strong alkaline medium, supporting Kraft process high pH and temperatures.

# Experimental

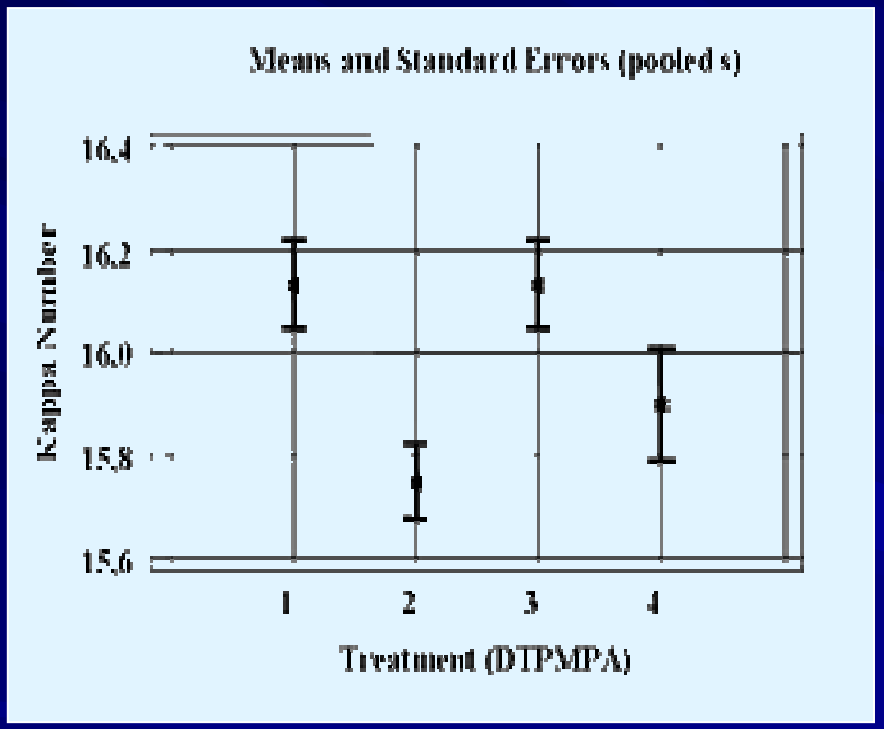
- *Eucalyptus spp.* air dried chips from Celulosa Argentina, Capitán Bermúdez mill, were used as raw material.
- Phosphonates were provided by Solutia Inc.
  - DTPMPA: (diethylene triamine penta (methylene phosphonic acid))
  - SPAP (Sodium salt solution of Polyaminophosphonic acids) is currently almost unknown for these uses.
- DTPMPA and SPAP were added in cooking and brown stock washing.
- Chelant agent charge of each stage was 0.1% (active acid base) on oven dry weight of chips or pulp respectively.

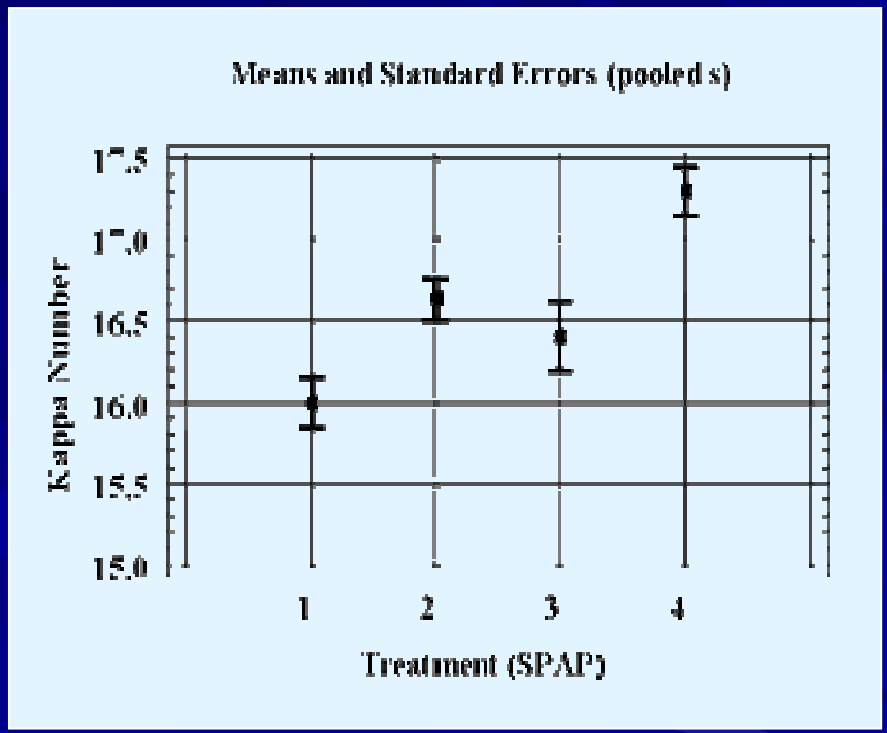
# Scheme of the experiences $2^2$ factorial design

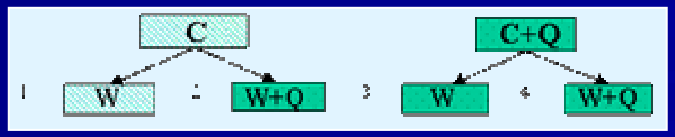



| Treatment | Q in cooking | Q in brown stock washing |
|---|---|---|
| 1 | Without Q | Without Q |
| 2 | Without Q | With Q |
| 3 | With Q | Without Q |
| 4 | With Q | With Q |

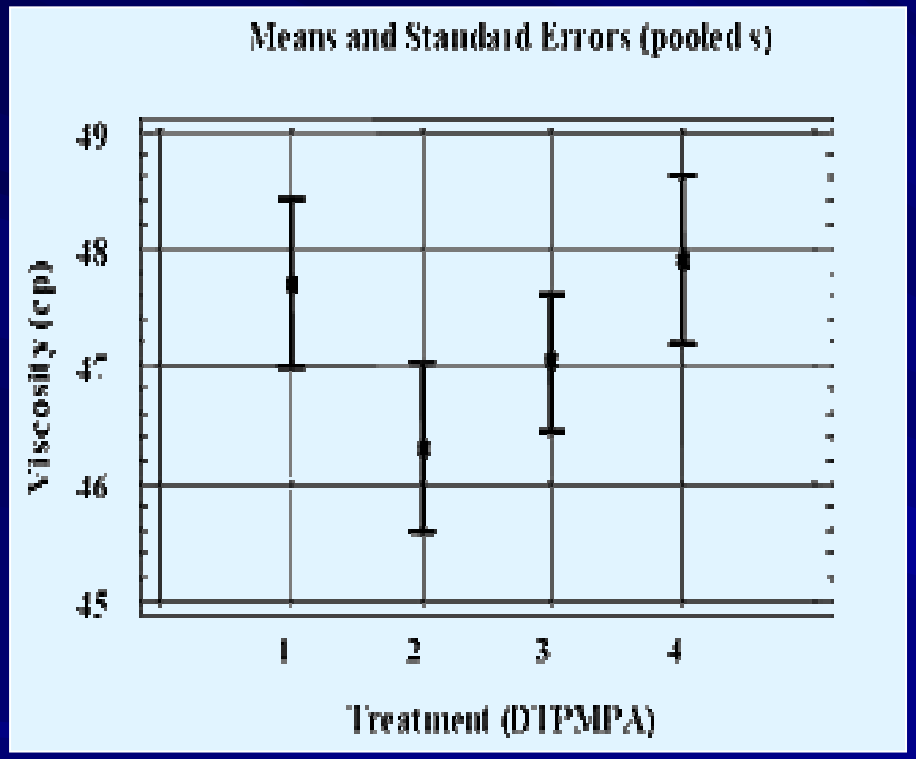
# Results DTPMPA -SPAP

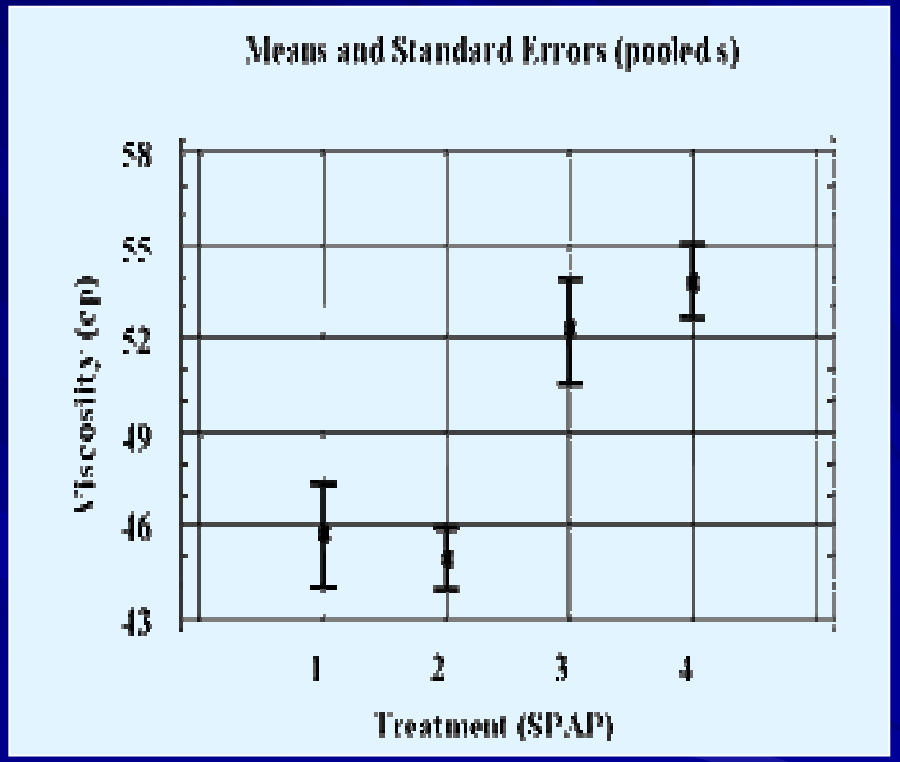


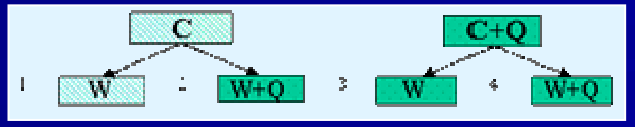



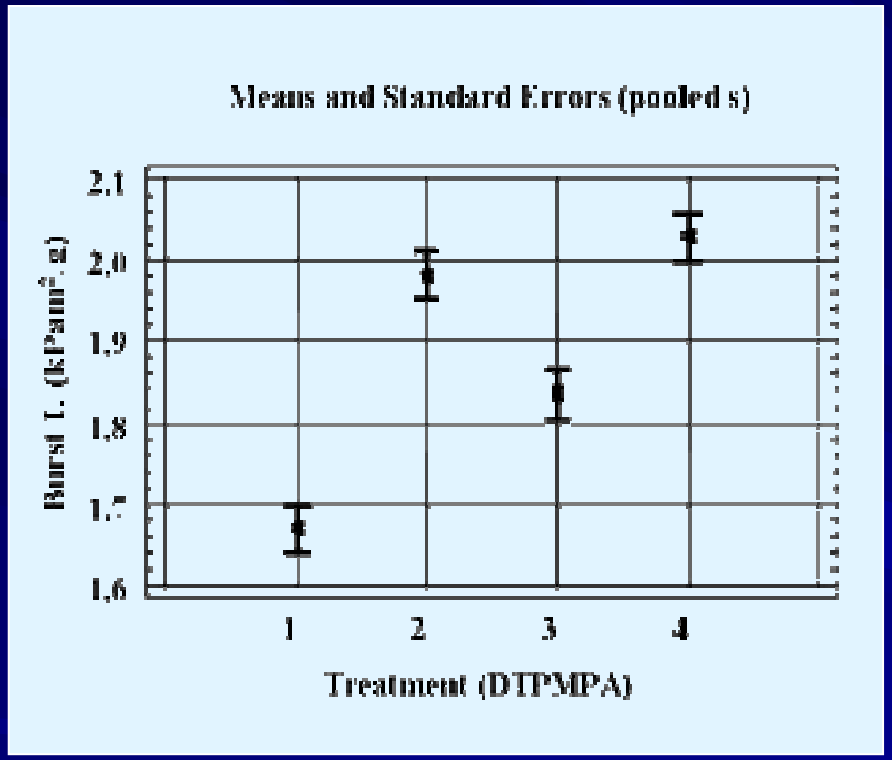
# Results DTPMPA -SPAP

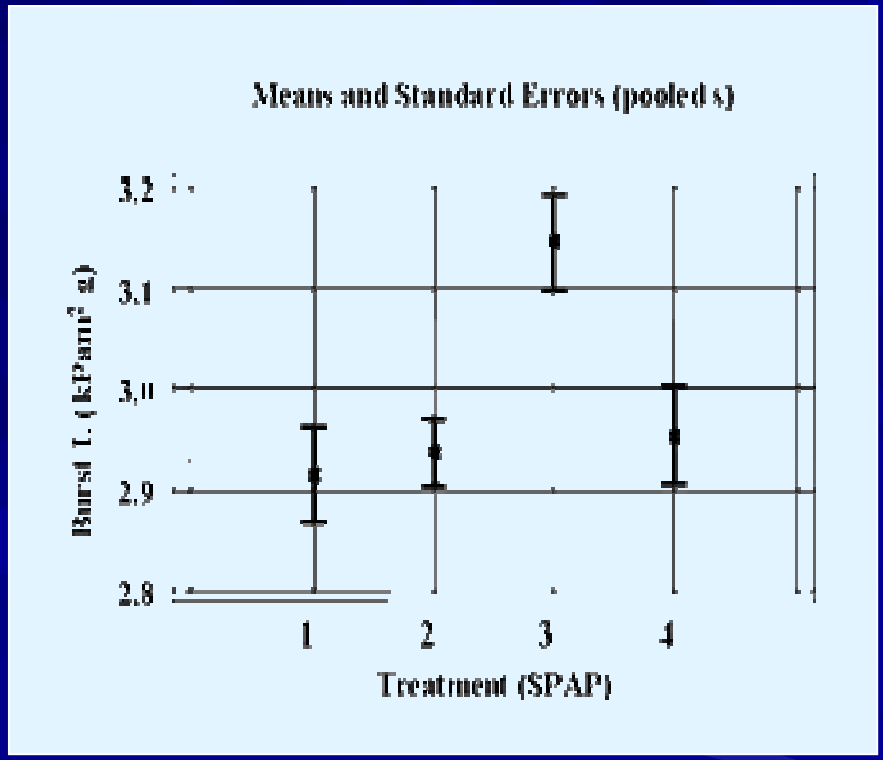


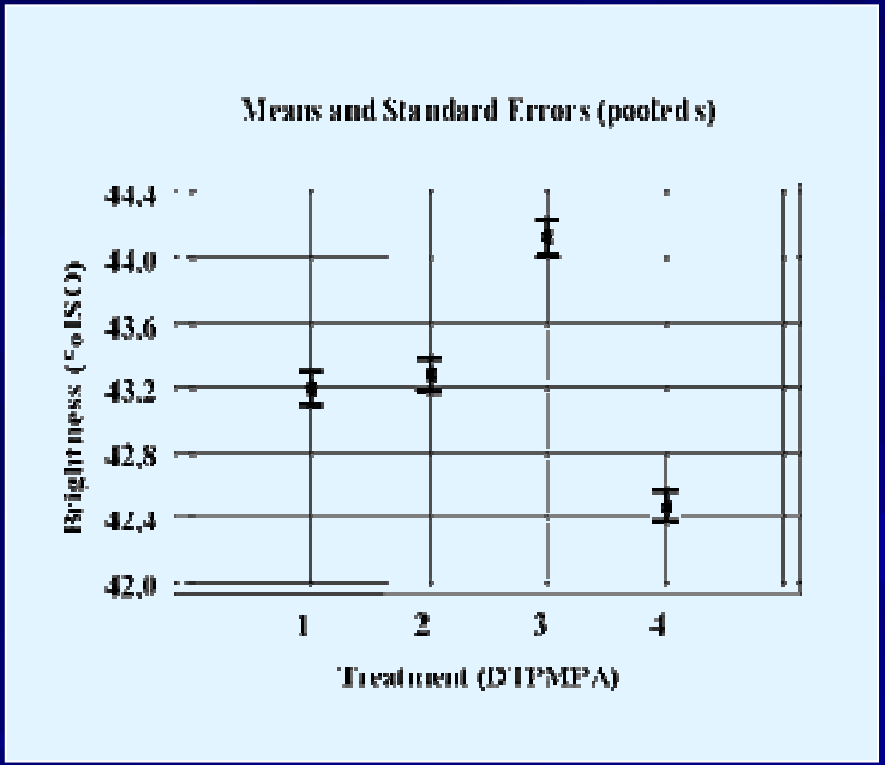



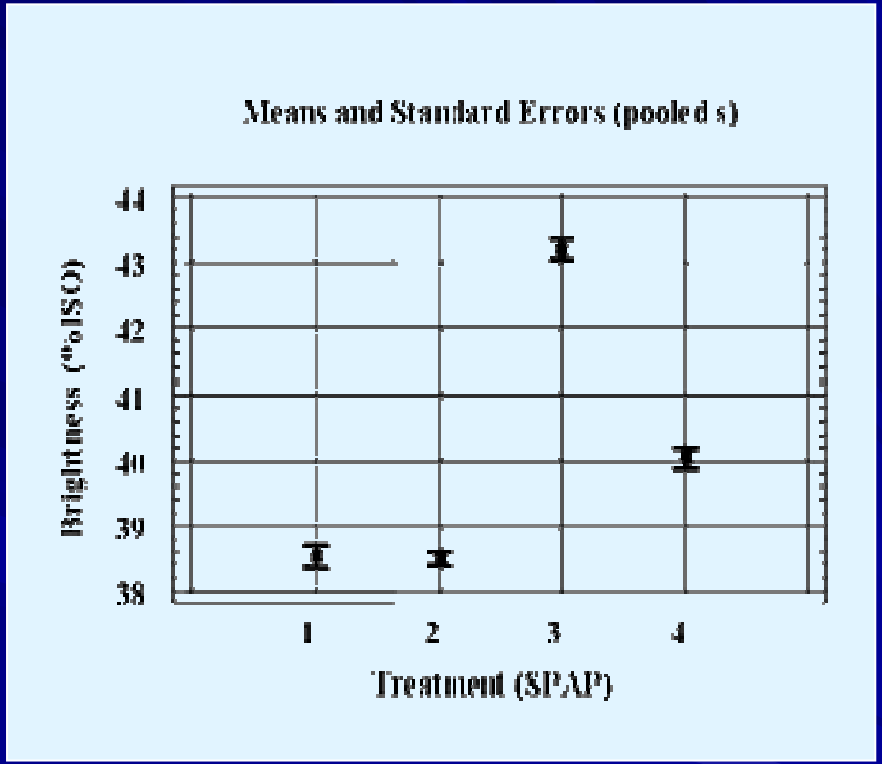
# Results DTPMPA



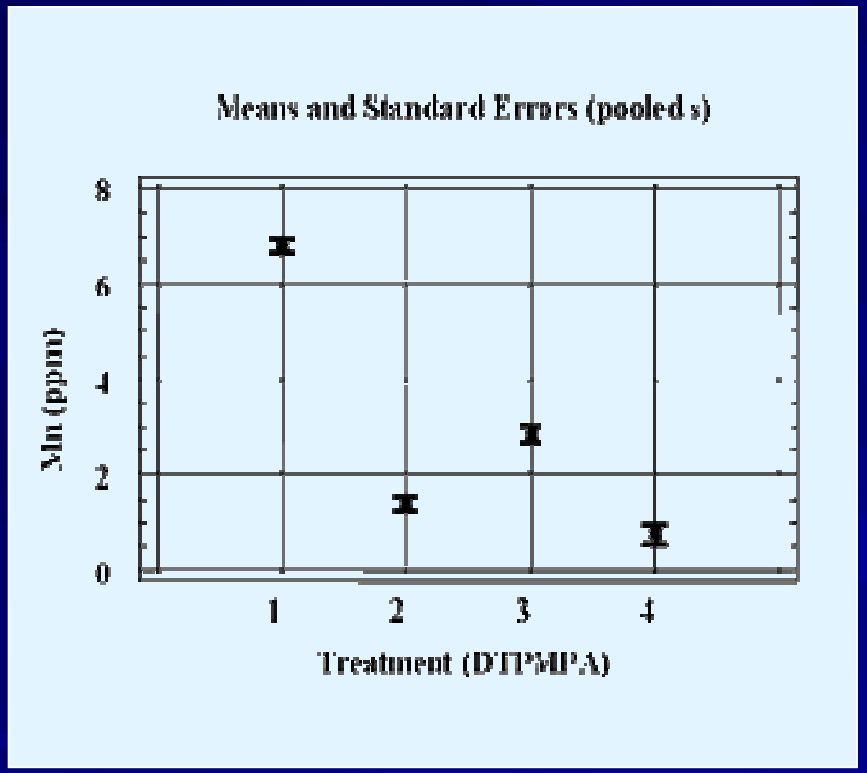



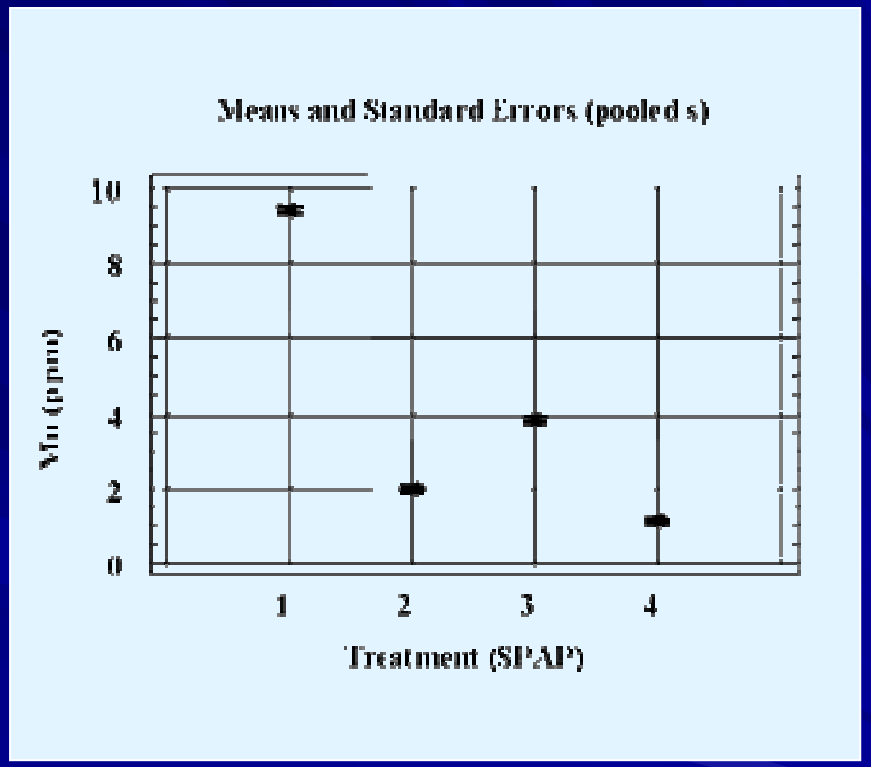

# Results DTPMPA - SPAP



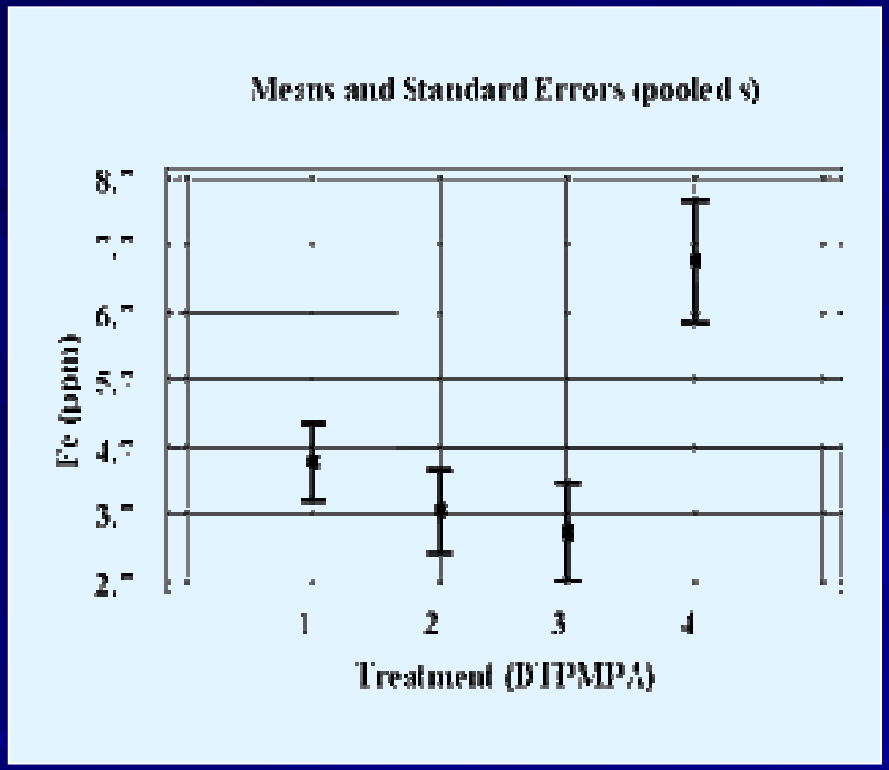



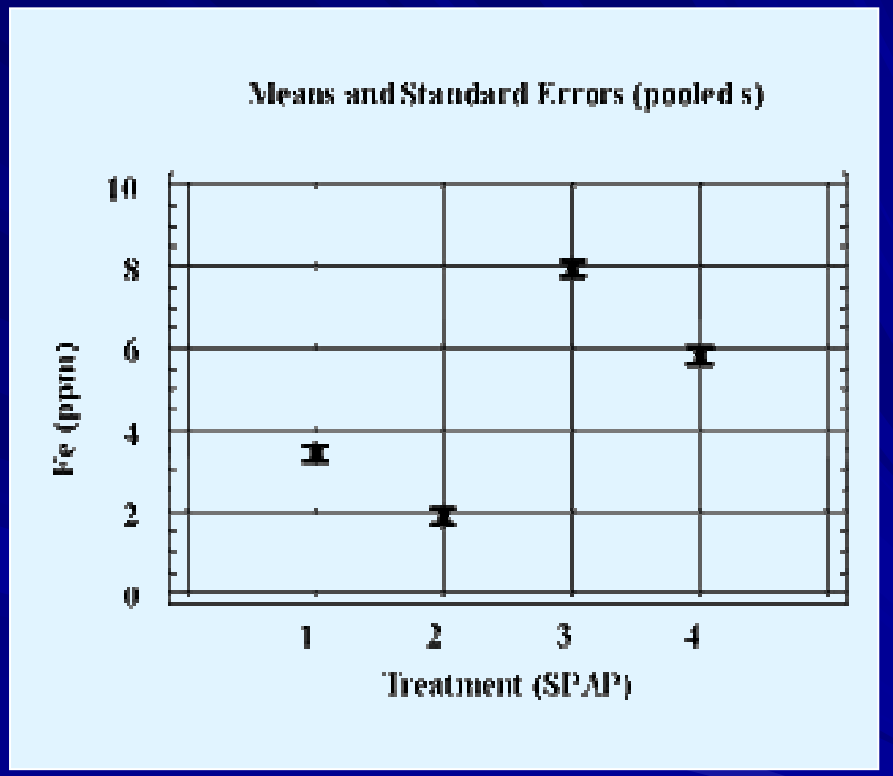

# Results DTPMPA




# Results DTPMPA




# Conclusions

- Chelant agents do not perform in the same way concerning *Eucalyptus spp.* Kraft pulps.
- Depending on mills particularities, and their diverse metallic ions concentration in wood and pulps, different strategies of metal management could be applied.

# Conclusions

- Adding phosphonates in cooking or in brown stock washing is a valid alternative to remove harmful ions.
- This option involves the use of new products that undergo high temperatures and pH.

# Conclusions

- Results show that metallic ions could be almost eliminated previous to the oxygen stage.
- DTPMPA addition in the cooking stage reduces Mn to a very low level, preserving or increasing physical properties.
- It is effective to reduce metallic ions when applied in brown stock washing, producing better levels of physical properties referred to the control (without any treatment).

# Conclusions

- SPAP shows a good performance in physical properties when applied in cooking with usual washing (without chelant), but metals are best removed when dosed in brown stock washing.
- In both cases, manganese is reduced to a very low level at the very beginning of the bleaching sequence.
- Mn levels after 0.1% of DTPMPA or SPAP addition in brown stock washing would be less than 2ppm.
- SPAP is more effective than DTPMPA in iron reduction and in magnesium preservation, resulting in highest viscosity levels.

# II. DIFFERENT CHELANT AGENTS ADDITION IN BROWN STOCK WASHING

# Introduction

- Most popular chelating agents in the pulp and paper industry are:
  - EDTA (ethylene diamine tetraacetic acid)
  - DTPA (diethylene triamine pentaacetic acid).
- Other sequesters included more recently are:
  - HEDTA (Hidroxyethylene diamine tetraacetic acid)
  - PHOSPHONATES:
    - DTPMPA: (diethylene triamine penta (methylene phosphonic acid))
    - HEDP (1-Hydroxy ethylidene diamine (1, 1-diphosphonic acid)).
    - SPAP (Sodium salt solution of Polyaminophosphonic acids) is currently almost unknown for these uses.

# Introduction

- An important aspect to consider in chelating agent selection is pulp pH.
  - EDTA requires acid conditions
  - DTPA, DTPMPA and HEDP function in alkaline medium.

# Introduction

- Hexenuronic acid groups, which consume electrophilic bleaching chemicals (chlorine dioxide, ozone and peracides), are usually eliminated using an acid treatment.
- They are however unreactive in alkaline oxygen and peroxide bleaching stages.
- In this case, the intermediate acid stage removal can reduce costs greatly.
- Hexenuronic acid groups can originate the low brightness stability of TCF pulps, so color reversal should be keep under observation.

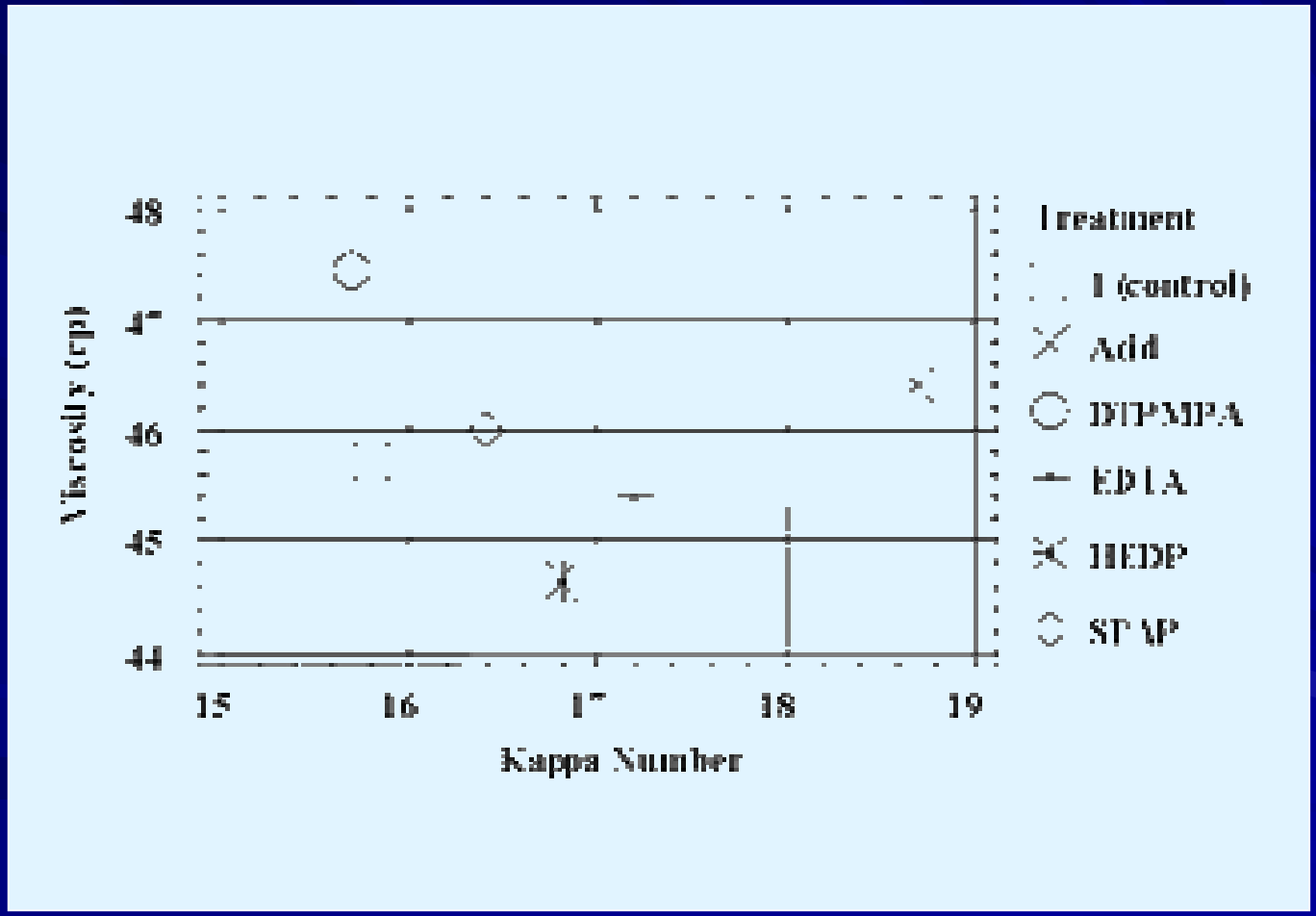
# Introduction

- This work shows alternatives of chelant application in *Eucalyptus* Kraft brown stock washing, preceding oxygen delignification and TCF bleaching.
- Phosphonates chelating agents known as DTPMPA, HEDP and SPAP were applied using EDTA and an acid stage as controls.

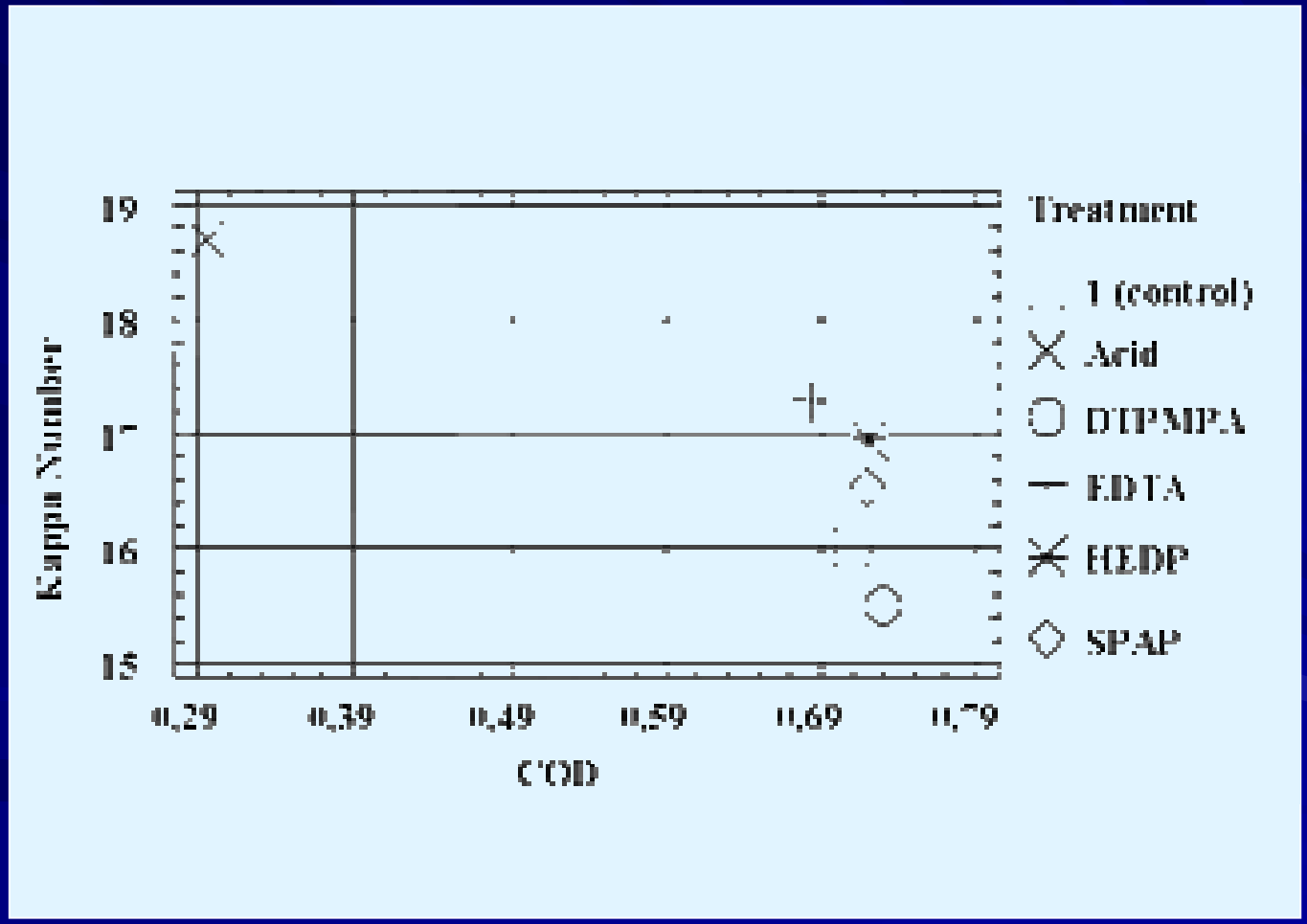
# Experimental

- Conditions were similar to those of part I.
- The work was carried out dividing one pulp in fractions, to assure equal starting conditions.
- Unscreened pulp yield was 50.6%.
- Washing was standardized to obtain similar COD values before de oxygen stage.
- Washing was accomplished in three stages.
- DTPMPA, SPAP, and HEDP, were added in the second brown stock washing stage.
- Acid treatments were applied in the third washing stage.

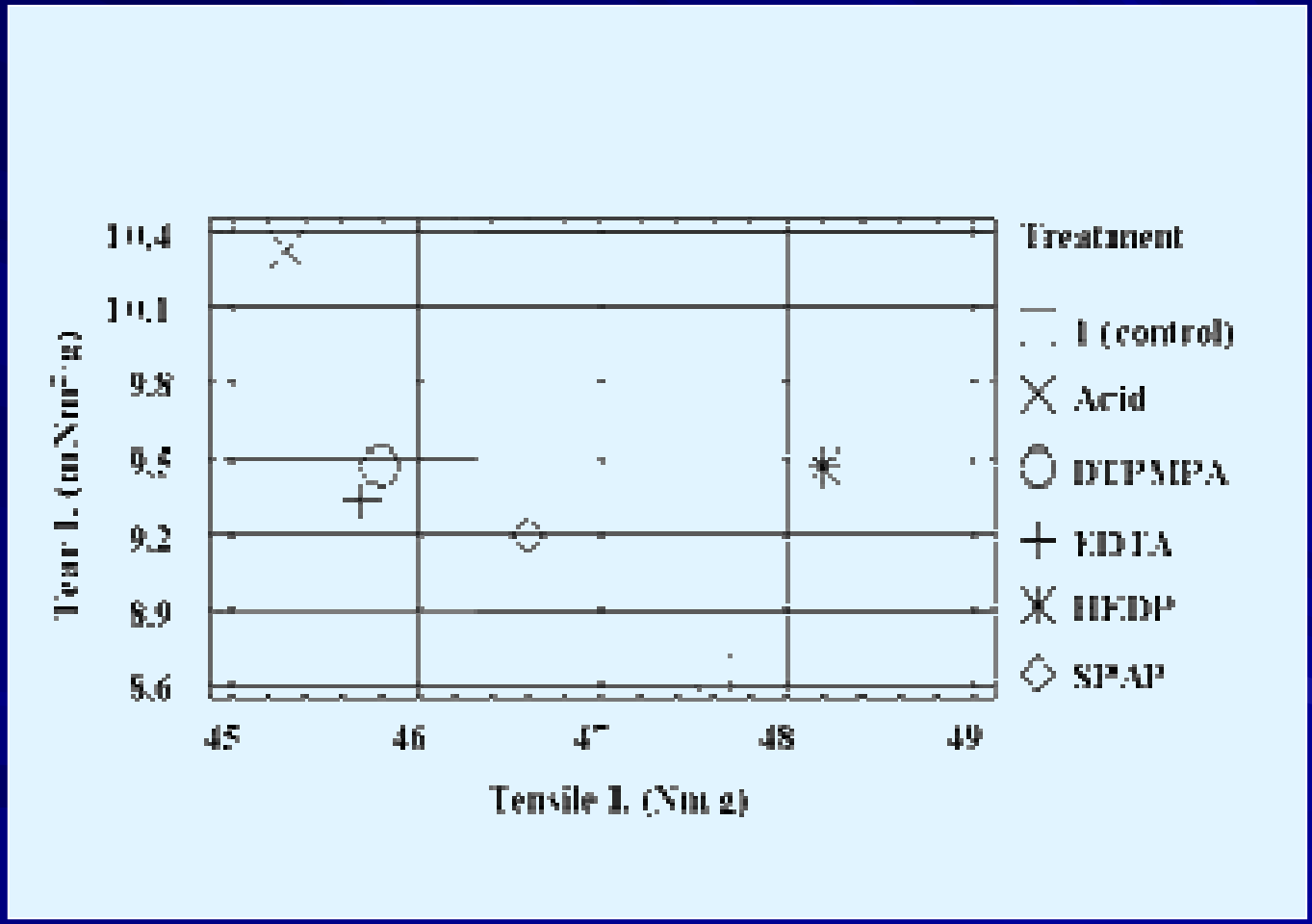
# Results


Viscosity (cp)
48
46
44
15
16
18
19
Kappa Number
Treatment
Acid
DTPMPA
EDTA
HEDP
STMP

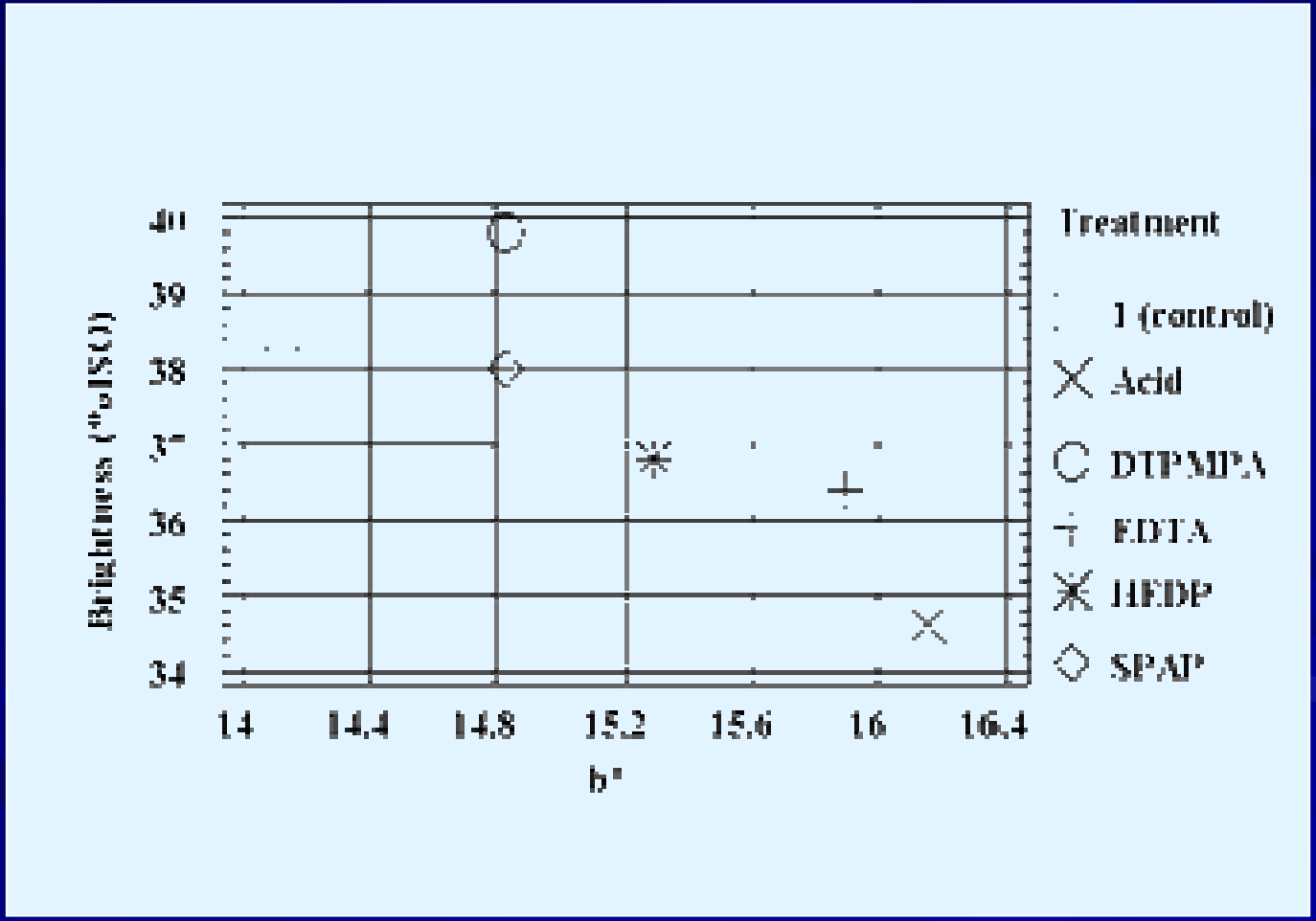
# Results


Kappa Number
19
18
17
16
15
0,29
0,39
0,49
0,59
0,69
0,79
COD
Treatment
1 (control)
Acid
DTPMPA
EDTA
HEDP
SPAP

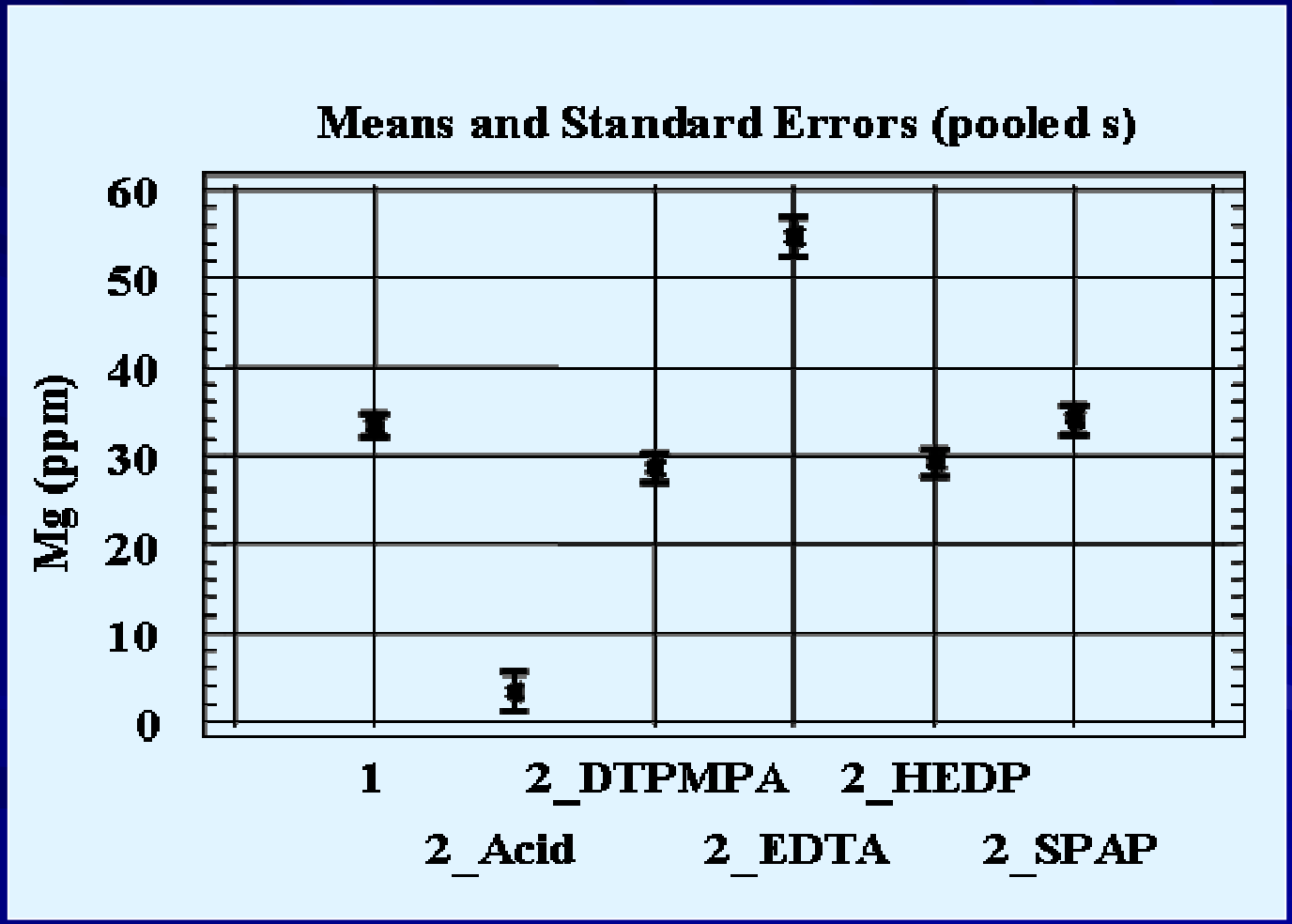
# Results


10.4
10.1
9.8
9.5
9.2
8.9
8.6
45
46
47
48
49
Tensile I. (Nm 2)
Treatment
I (control)
Acid
DETMPA
EDTA
HEDP
SPAP

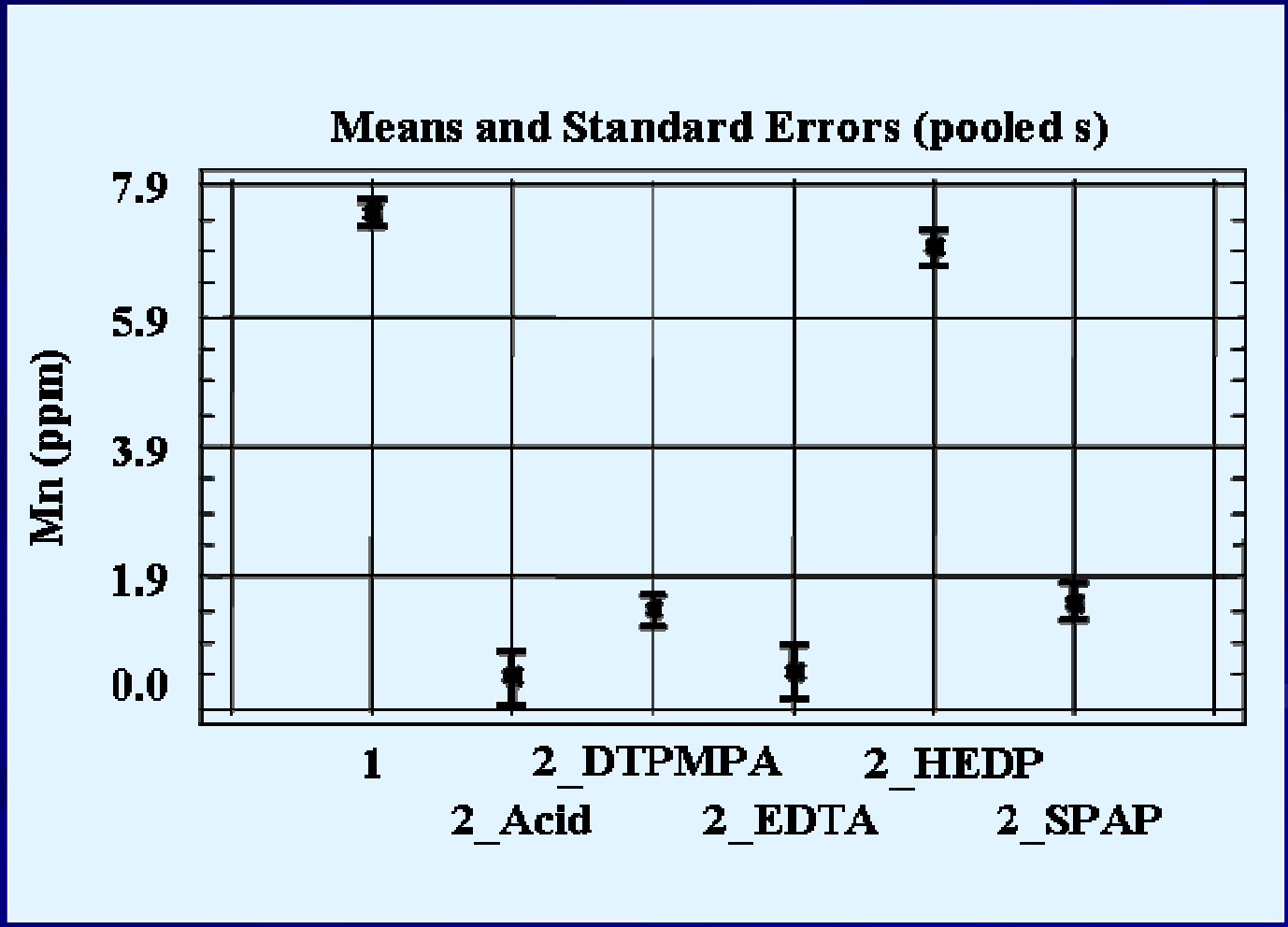
# Results


40
39
38
37
36
35
34
14
14.4
14.8
15.2
15.6
16
16.4
b*
Treatment
1 (control)
Acid
DTPMPA
EDTA
HEDP
SPAP

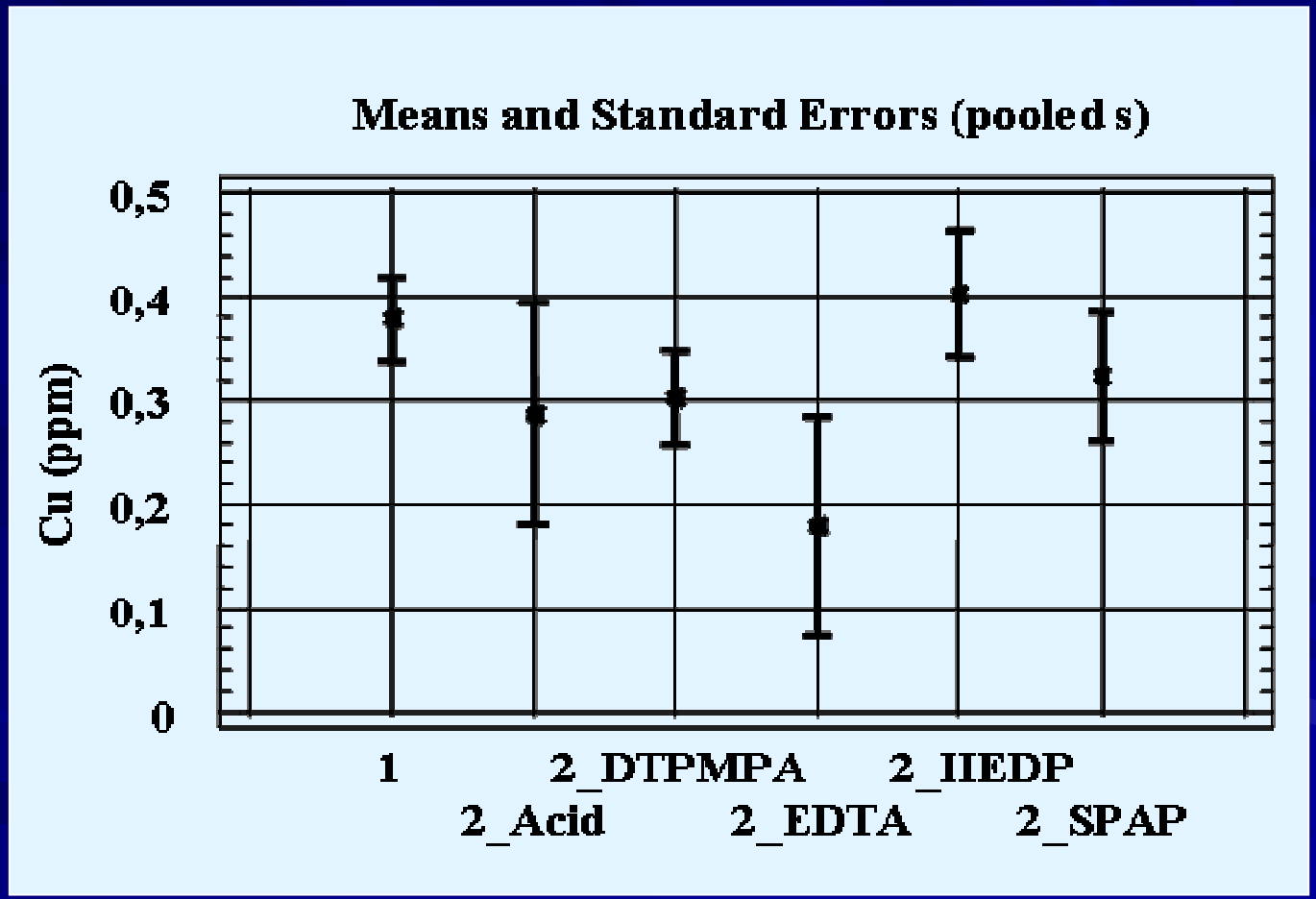
# Results


Means and Standard Errors (pooled s)
Mg (ppm)
60
50
40
30
20
10
0
1
2_Acid
2_DTPMPA
2_EDTA
2_HEDP
2_SPAP

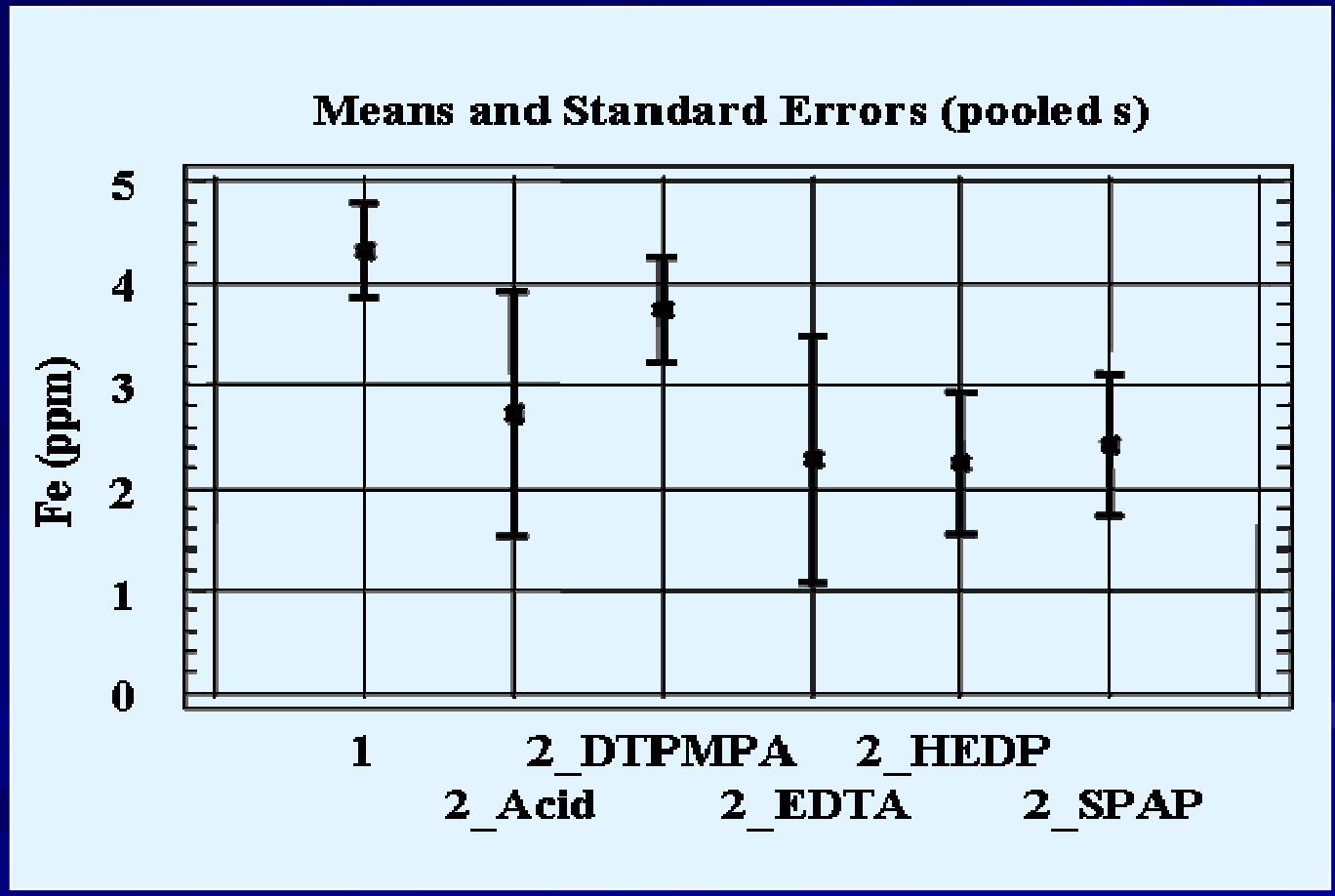
# Results


Means and Standard Errors (pooled s)
Mn (ppm)
7.9
5.9
3.9
1.9
0.0
1
2_DTPMPA
2_HEDP
2_Acid
2_EDTA
2_SPAP

# Results


Means and Standard Errors (pooled s)
Cu (ppm)
0,5
0,4
0,3
0,2
0,1
0
1
2_Acid
2_DTPMPA
2_EDTA
2_IIEDP
2_SPAP

# Results


Means and Standard Errors (pooled s)
Fe (ppm)
5
4
3
2
1
0
1
2_DTPMPA
2_HEDP
2_Acid
2_EDTA
2_SPAP

# Conclusions

- Chelant agents do not perform in the same way concerning *Eucalyptus spp.* kraft pulps.
- Depending on the particular problem of the mill and its different metallic ions concentration, diverse strategies of metal management could be applied.
- Phosphonates incorporation in brown stock washing is a valid choice.
- Results show that metallic ions could be almost eliminated before the oxygen stage.

# Conclusions

- Acidic treatments require an intermediate stage involving sulfuric acid addition.
- The consequence is supplementary manipulation and equipment costs, including special materials.
- These reasons make expensive its utilization.

# Conclusions

- Even though an acidic washing at pH= 2 seem to have benefits in ions reduction, lignin precipitation onto fibers makes unviable its application.
- In this case, washing efficiency reduces, as revealed by Kappa number increase and COD reduction.
- This effect could be harmful to the following oxygen stage.

# Acknowledgements


- This work is part of the “Best Chelating Agents Management to Obtain TCF Kraft Bleached Pulps” applied research project financed by Solutia Inc.
- Mr. Sheldon Verret of Solutia Inc. is gratefully acknowledged for reviewing the manuscript.
- **Technical team**: S.E. Aguilar; O.M. Barboza; D.I. Bengoechea; J. Clermont; P. Meza; C.A. Pavlik; S. Wolfart.