# *A comparison of electron paramagnetic resonance (EPR) spectroscopy with other staling indices to assess the impacts of brewhouse gallotannin addition on beer flavour stability*

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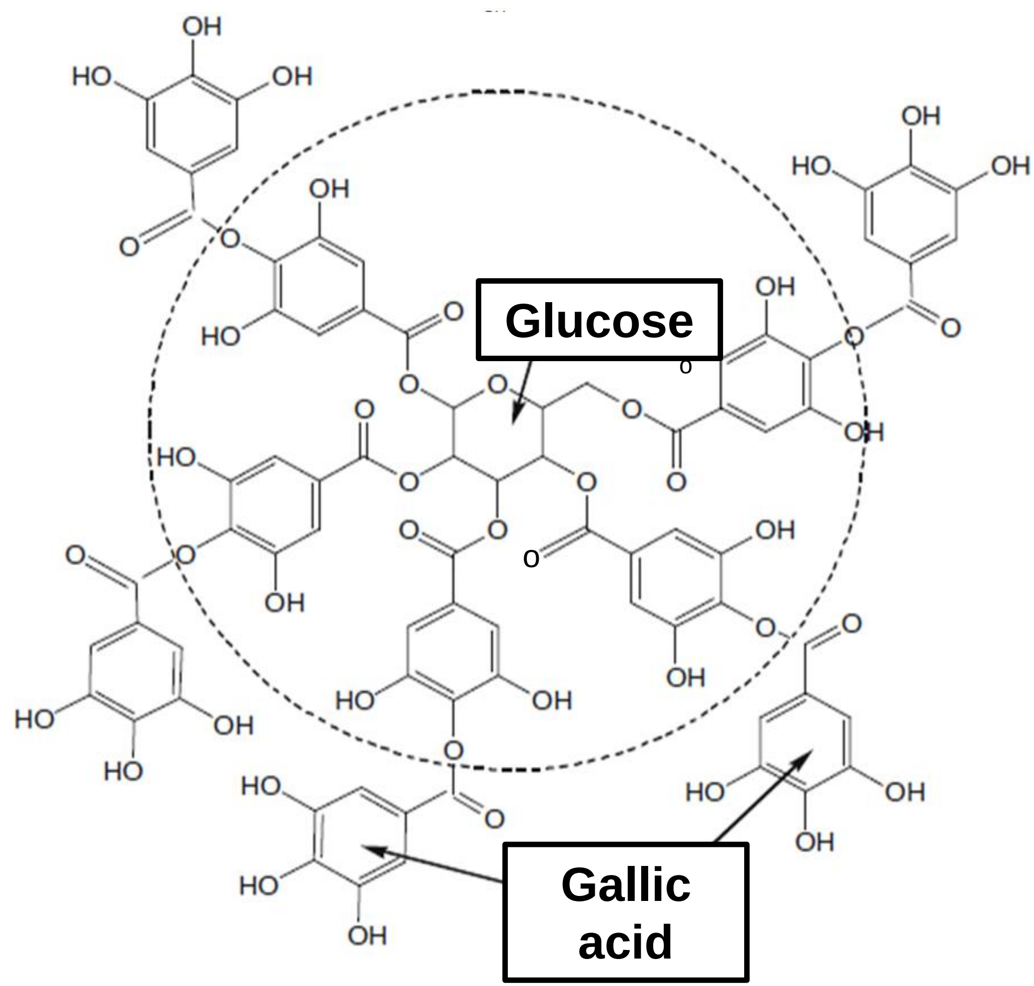
# Overview

- Introduction & hypothesis of research
- Trial design and analytical methods
  - Pilot scale trials (16 hl)
  - Large scale trials (1500 hl)
- Results
- Conclusions

# Introduction

- **Gallotannins (GT**
  **brewing**
  - Naturally sourced
    gallnuts
  - Hydrolysable tann
  - Glucose core surr
    gallic acid



# Hypothesis

- **How might gallotannins (GT) influence beer flavour stability?**
  - Ability to chelate metal ions (especially Fe(II))
  - Radical scavenging ability
  - Reduced formation of staling aldehydes and staling aldehyde precursors

# Trial design - Pilot scale

- High Gravity Lager-style beer (16°P)
- Three different trial 16 hl brews
  - Control with no addition
  - Mash conversion vessel (CV) addition of 3g/hl finished beer (FB) at mashing in
  - Wort kettle addition of 2.5 g/hl FB at 10 min before the end of boil
- Evaluate the effects of the gallotannin additions at key points of the process and in the final product

# Trial design
# Full-scale brewing trials

- Used same recipe and GT dosing regime as for pilot scale trials
- 1500 hl per brew, 1.5 or 3 brews to fill one fermenter, respectively
- 2 controls, 2 mash CV additions, and 1 wort kettle addition runs produced into final packaged beer
- Storage trial over 9 months at 20°C

# Analytical methods

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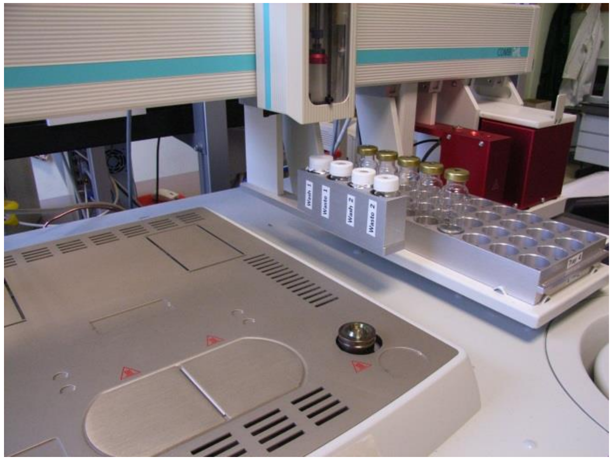
- Staling aldehydes via solid phase micro extraction (SPME)-GC-MS with on fibre derivatization
  - Derivatization agent PFBOA
  - Extraction time of 60 min at 50°C
- Thiobarbituric acid index (TBI)
  - Spectrophotometer reading absorption at 448nm
- Sulphur dioxide determined by distillation method
  - NaOH (0.1 mmol)

# Analytical methods (2)

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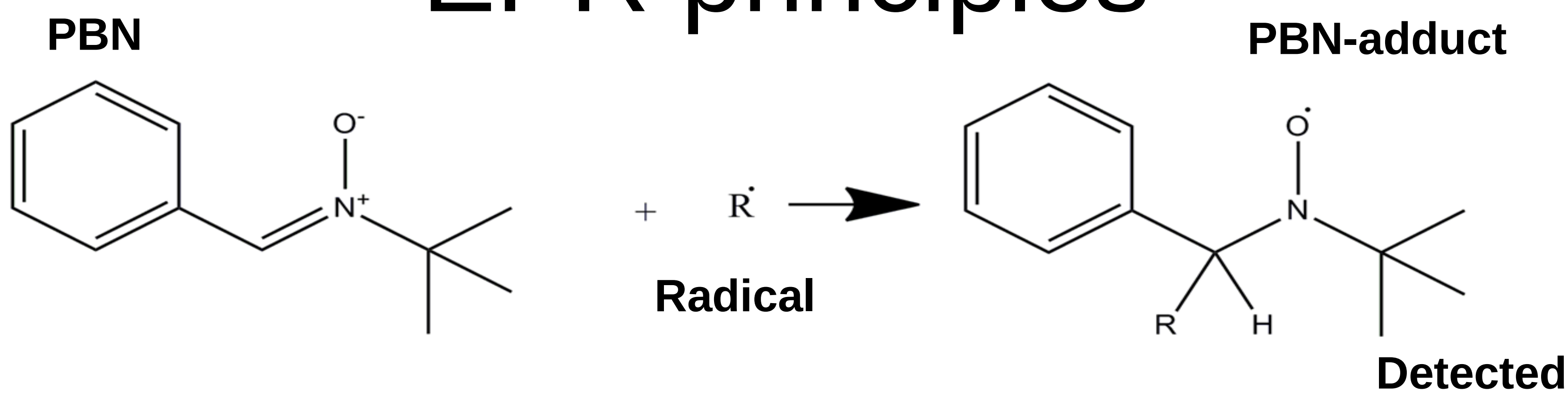
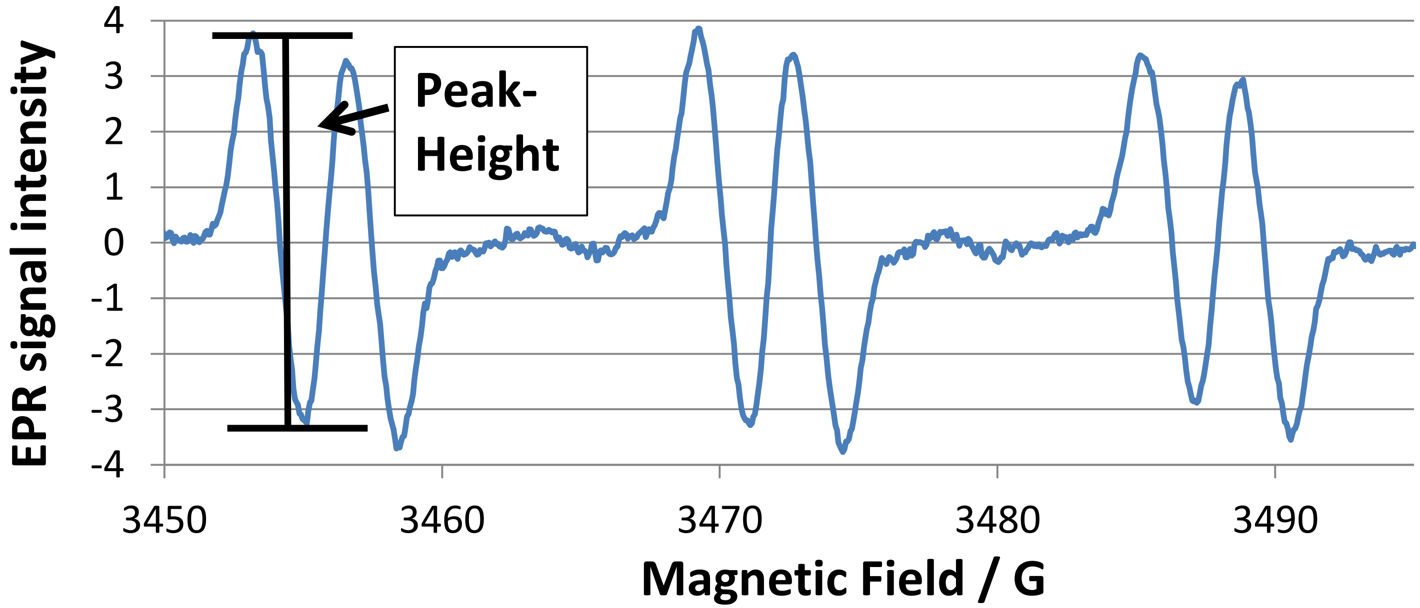
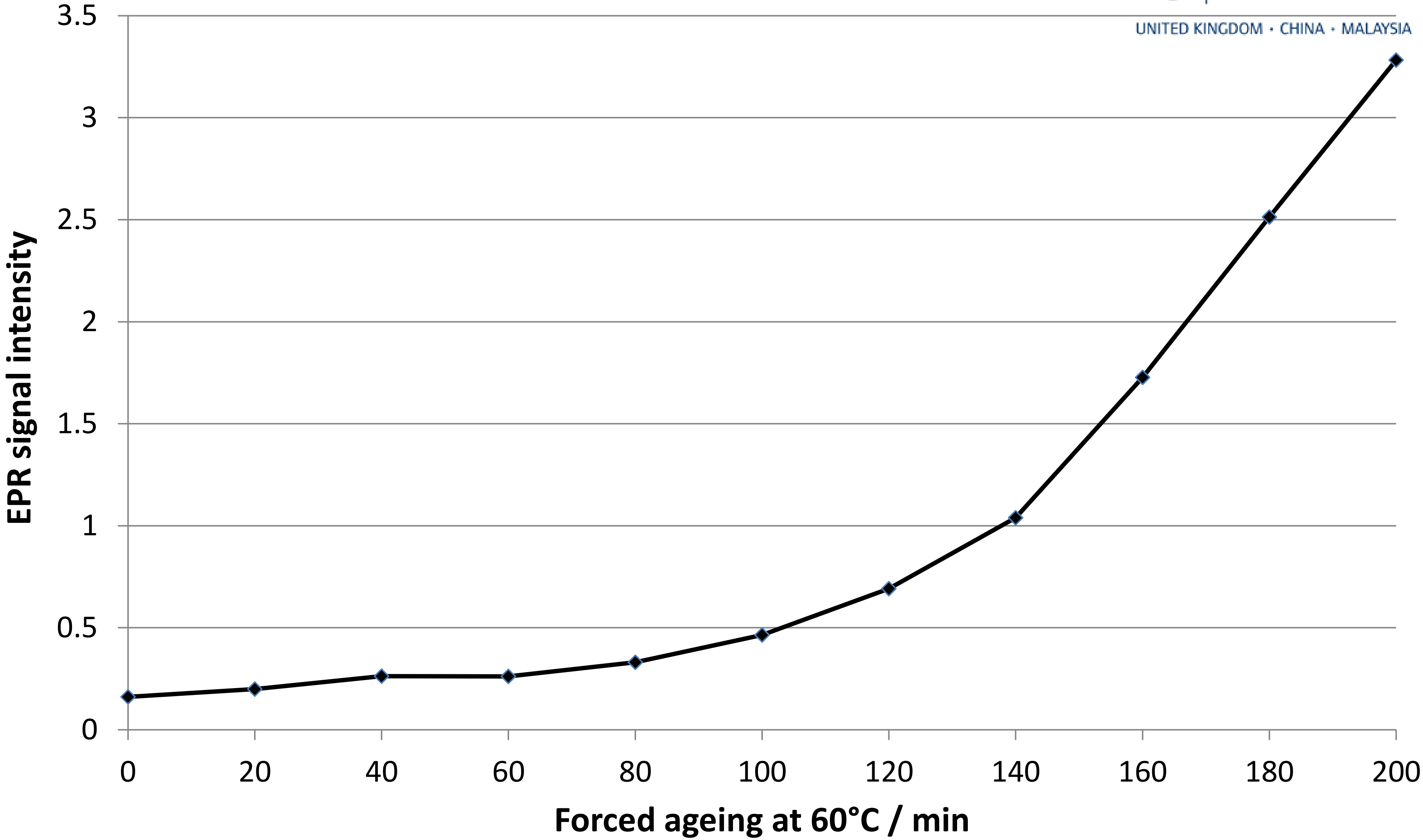
- Metal ion content determined by inductively coupled plasma mass spectrometry (ICP-MS)
  – Samples diluted 1/10 with nitric acid (2%)
- Sensory analysis
  – Expert brewery tasting panel consisting of 9 to 11 tasters
- EPR Antioxidant potential (Area)
  – PBN spin trap (50 mmol)
  – Forced ageing at 60°C for 200 min

# EPR principles



# EPR metric



3.5
3
2.5
2
1.5
1
0.5
0
0
20
40
60
80
100
120
140
160
180
200
EPR signal intensity
Forced ageing at 60°C / min

# EPR metric - Lag time

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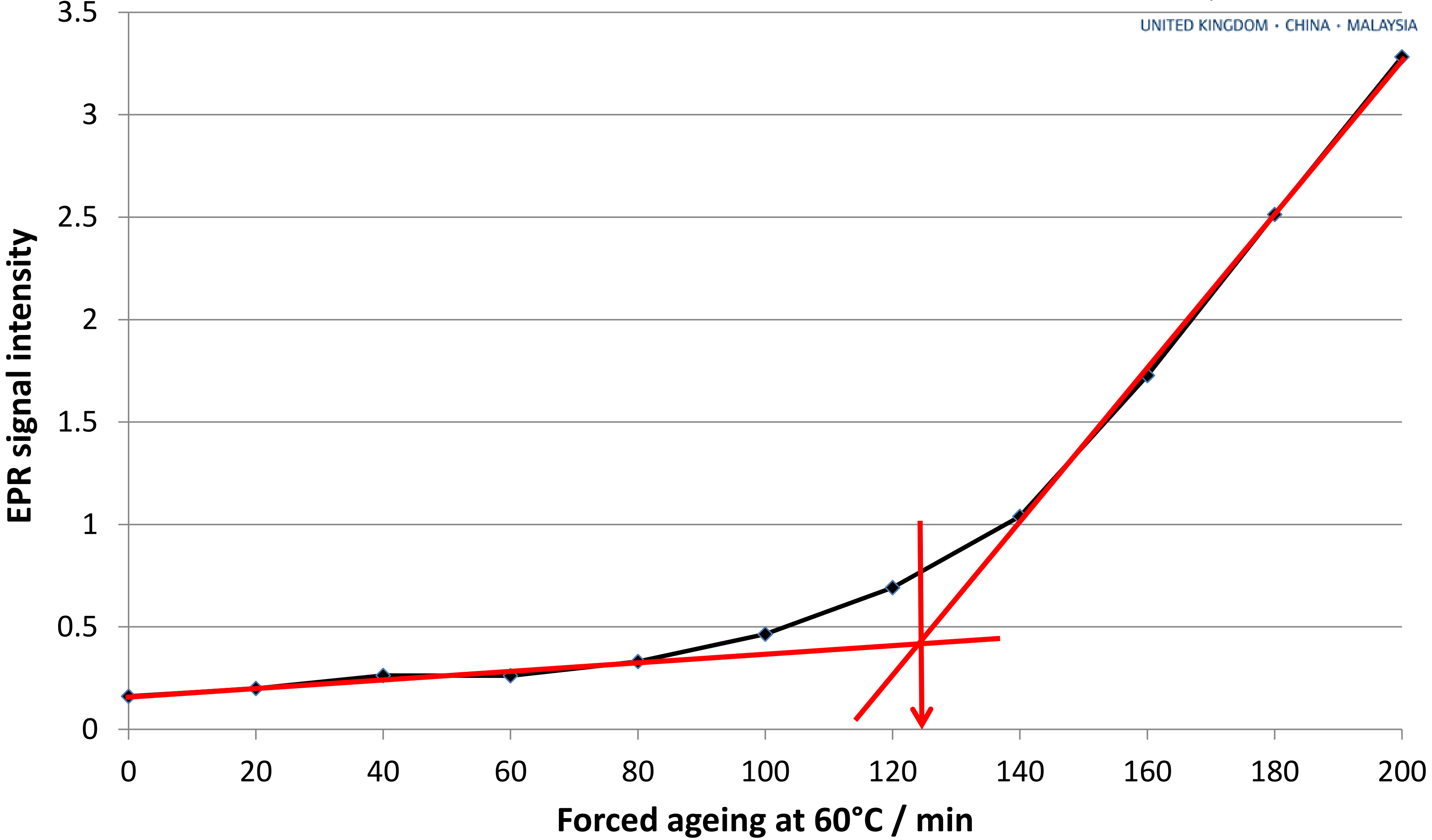


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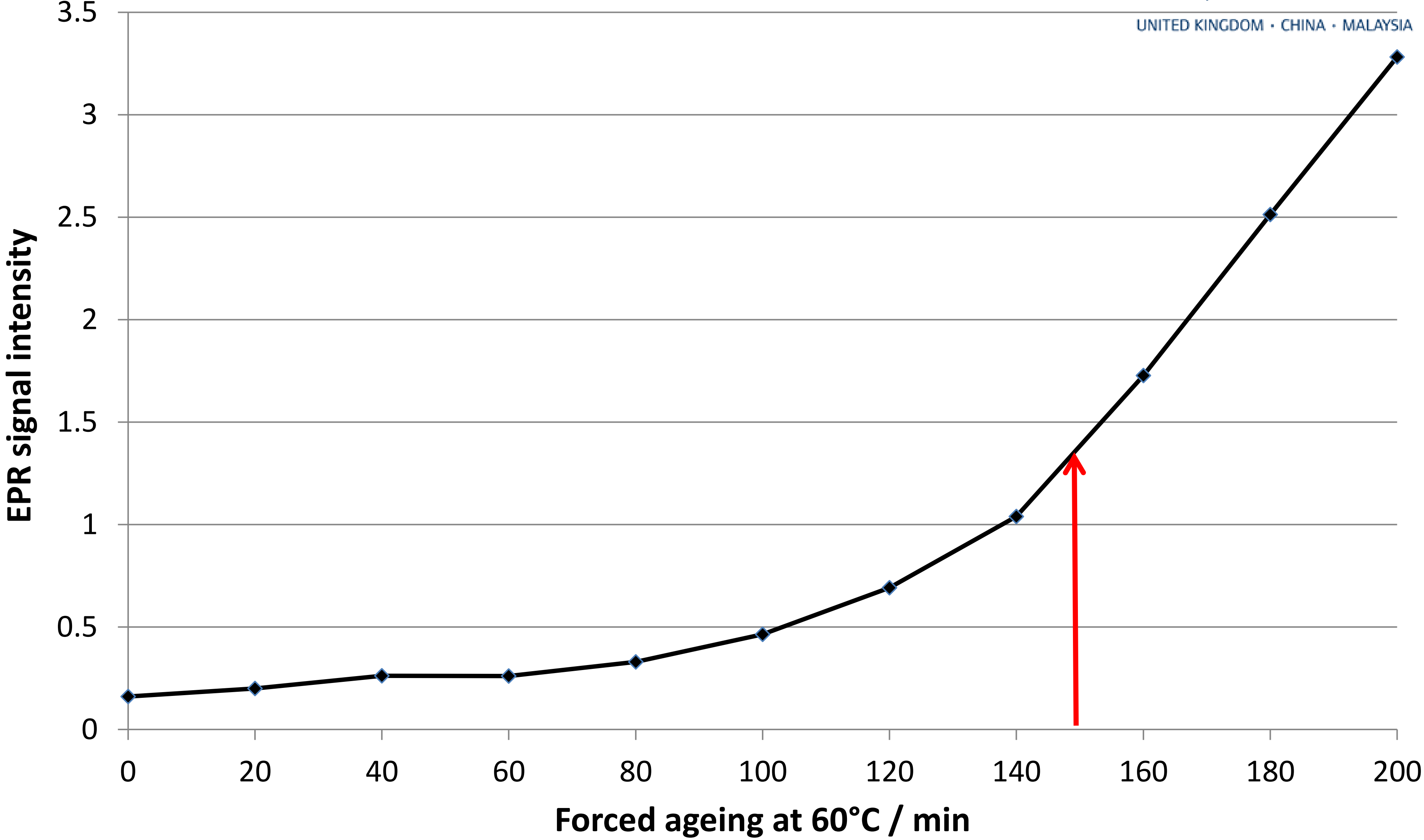
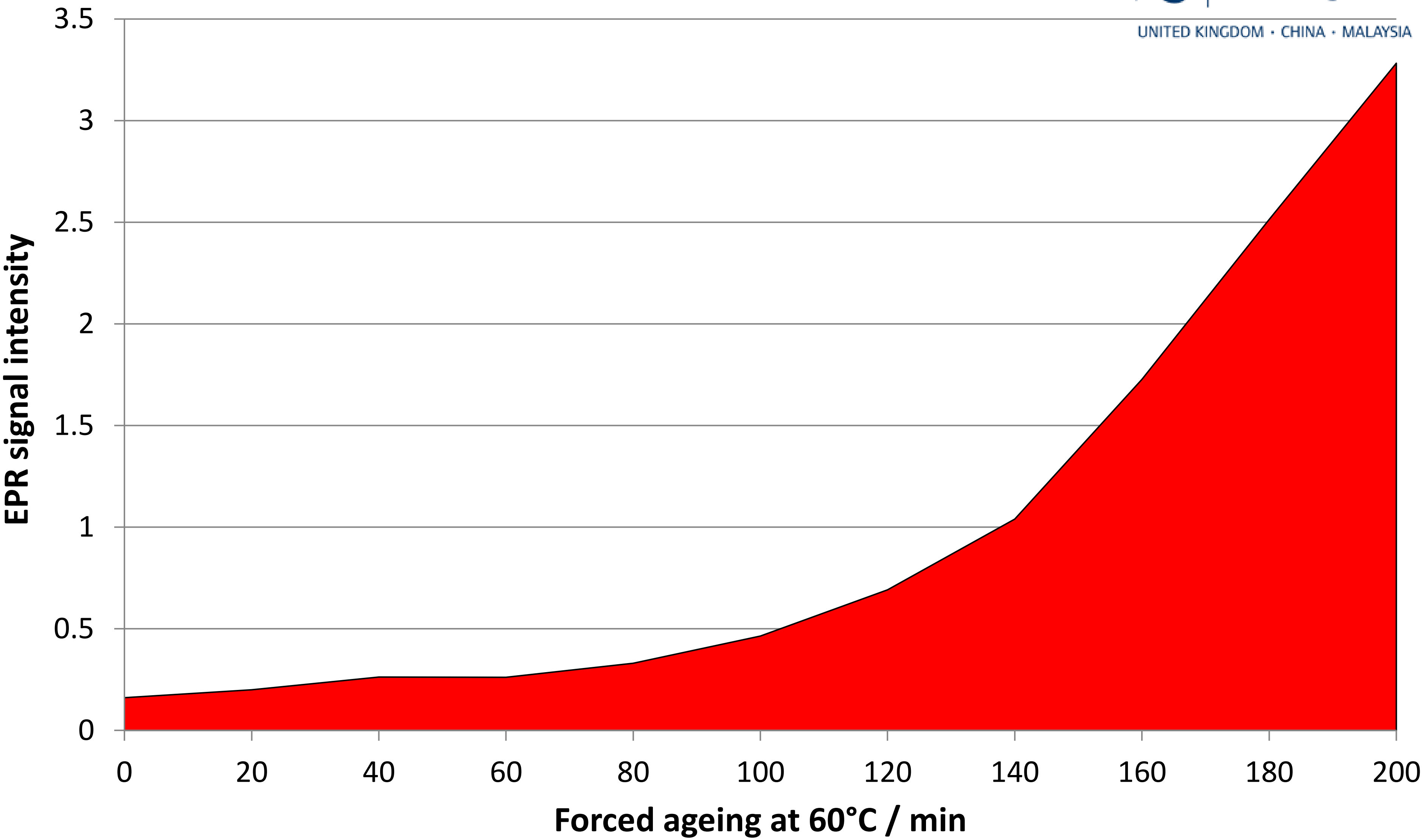
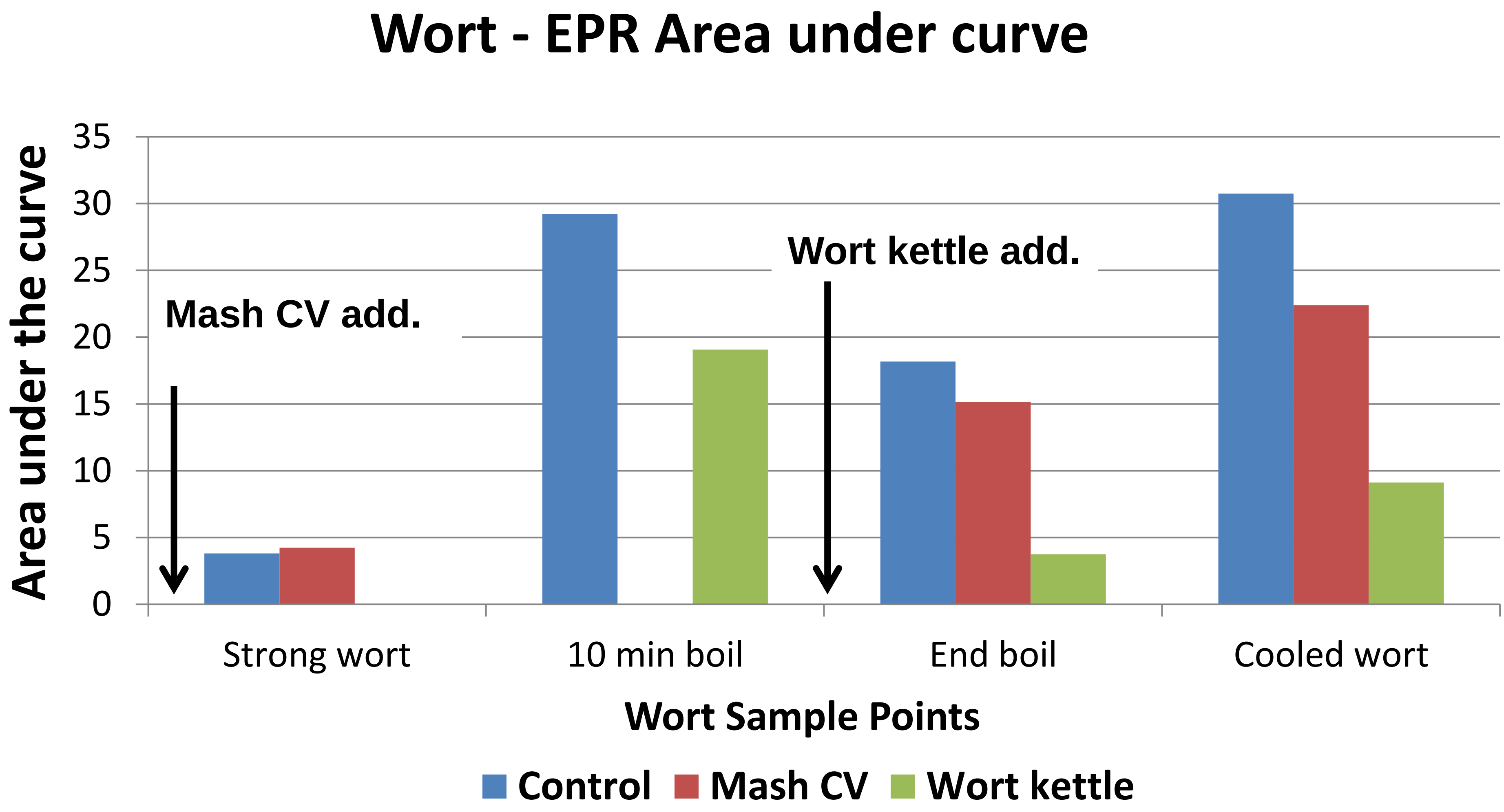
# EPR metric - $T_{150}$



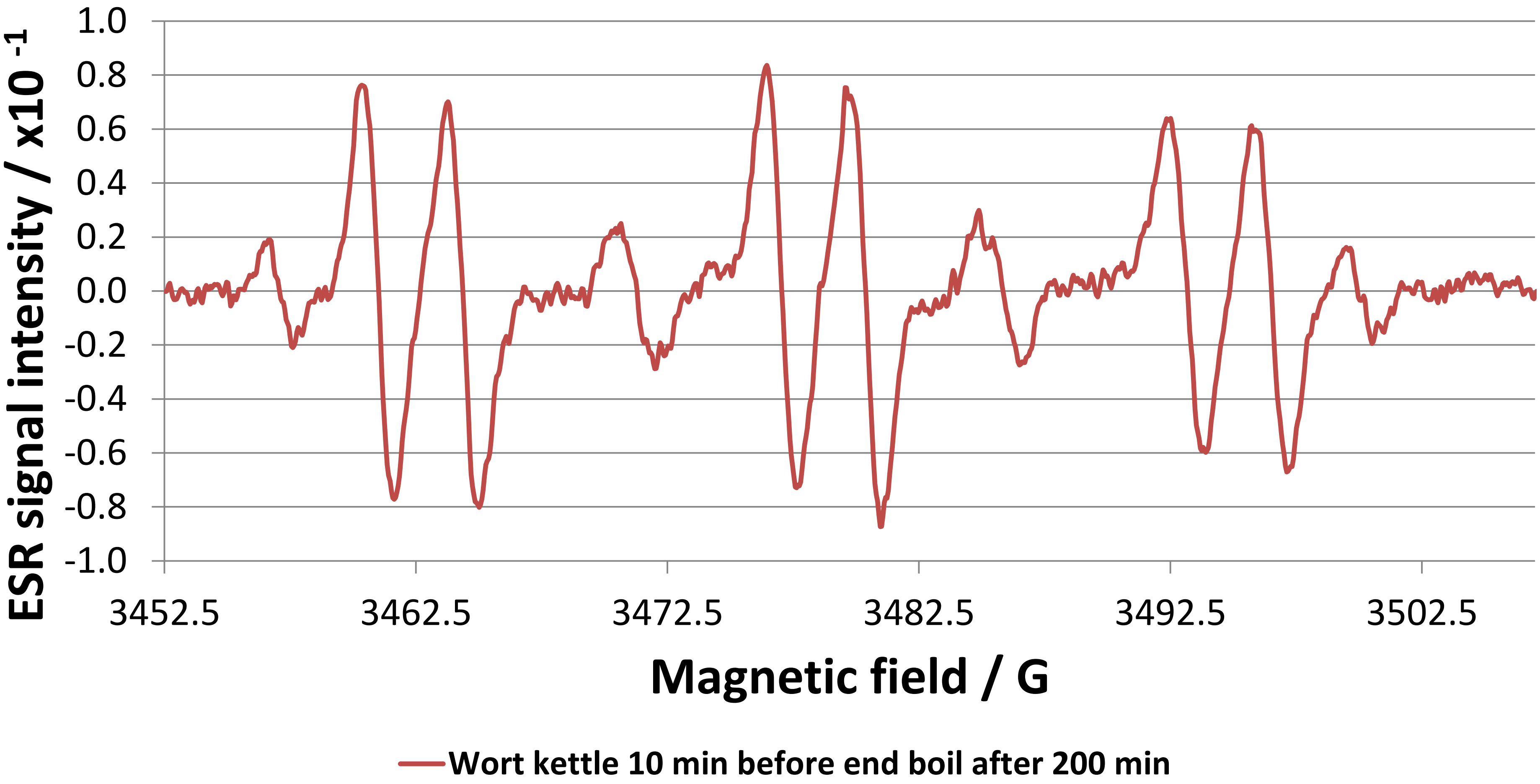
# EPR metric - Area



# Results – Pilot scale



# Comparison of EPR peak intensity (free radicals) of GT wort kettle addition before and after the addition of GT



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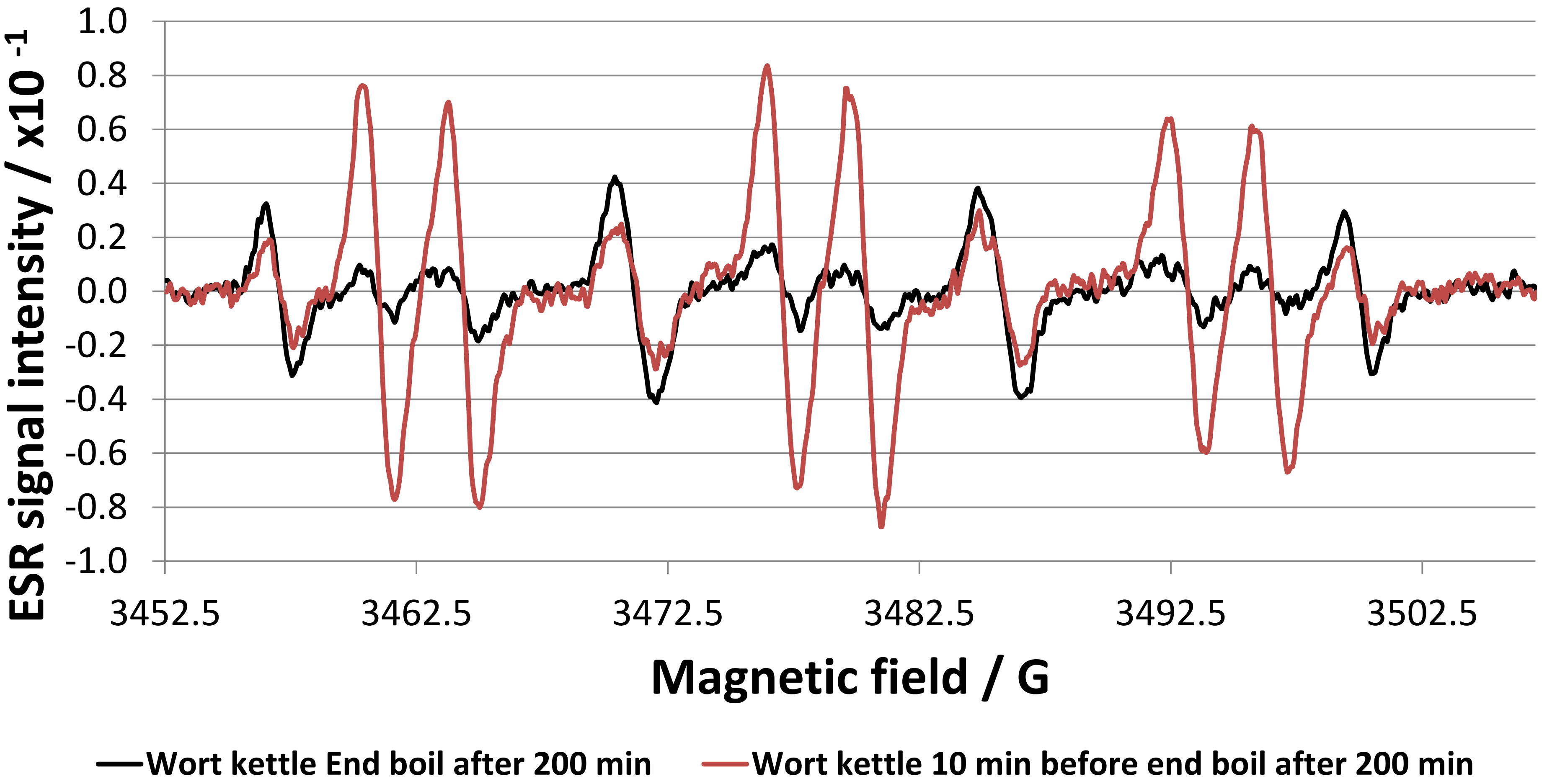

# Thiobarbituric acid index (TBI)

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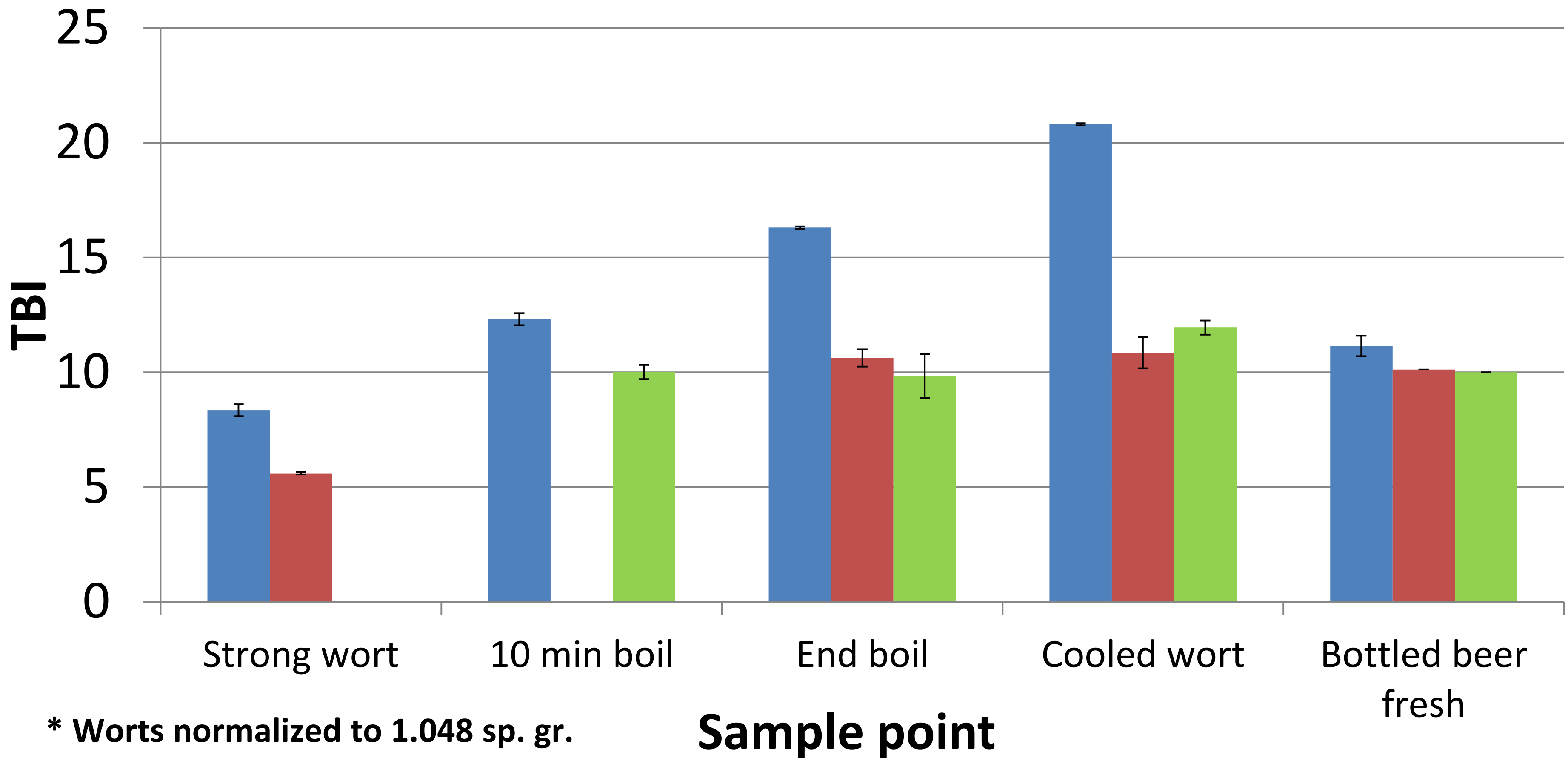
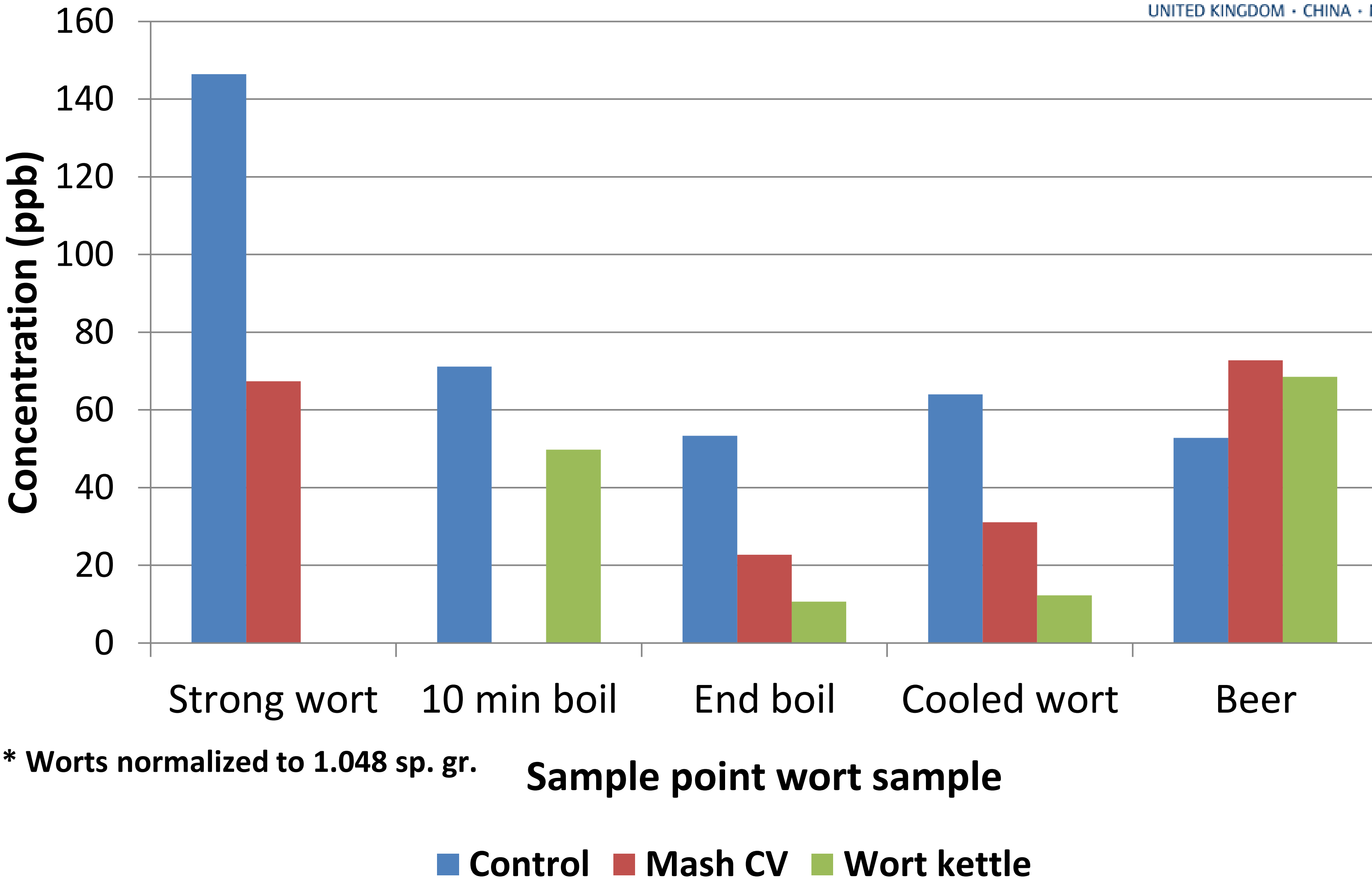



* Worts normalized to 1.048 sp. gr.

# Fe-levels (ppb)




* Worts normalized to 1.048 sp. gr.

# Summary – Pilot scale

- Both Mash and Wort Kettle GT addition **improved the oxidative stability of the wort**
- Mash and Wort Kettle GT additions showed essentially the **same benefits at Cooled Wort** as measured by TBI and EPR metrics
- **GT addition substantially reduced iron levels** in cooled, clarified wort as validated by ICP-MS

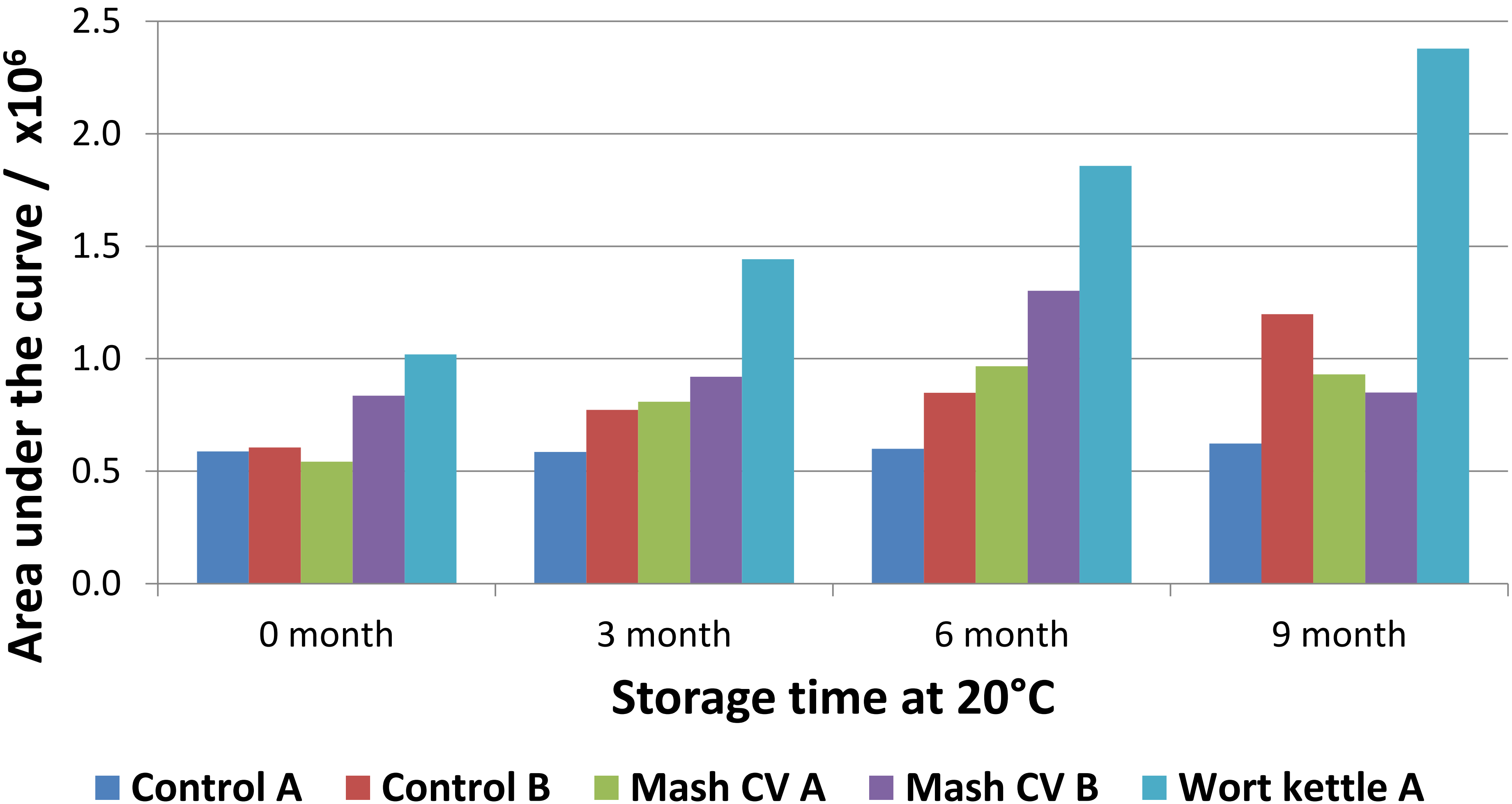
# Summary – Pilot scale

- The **benefits observed in Cooled Wort from GT additions were negated by high Fe pick-up** during the brewing process to packaged beer

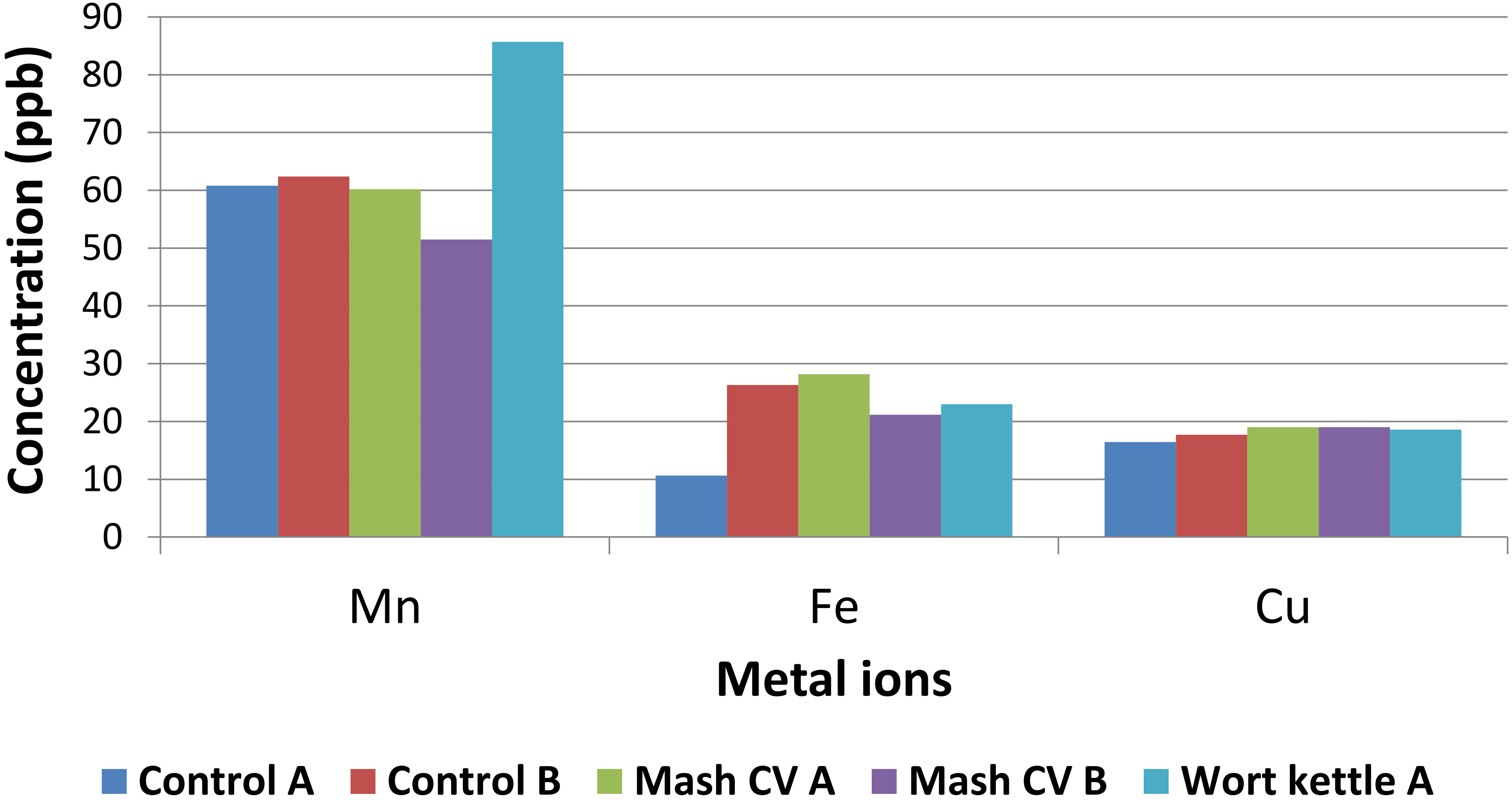
- Also the **reducing power of the yeast** during fermentation could have moderated the benefits of GT addition observed in the TBI of cooled wort

**→ Trials repeated at full-scale using the same addition regime**

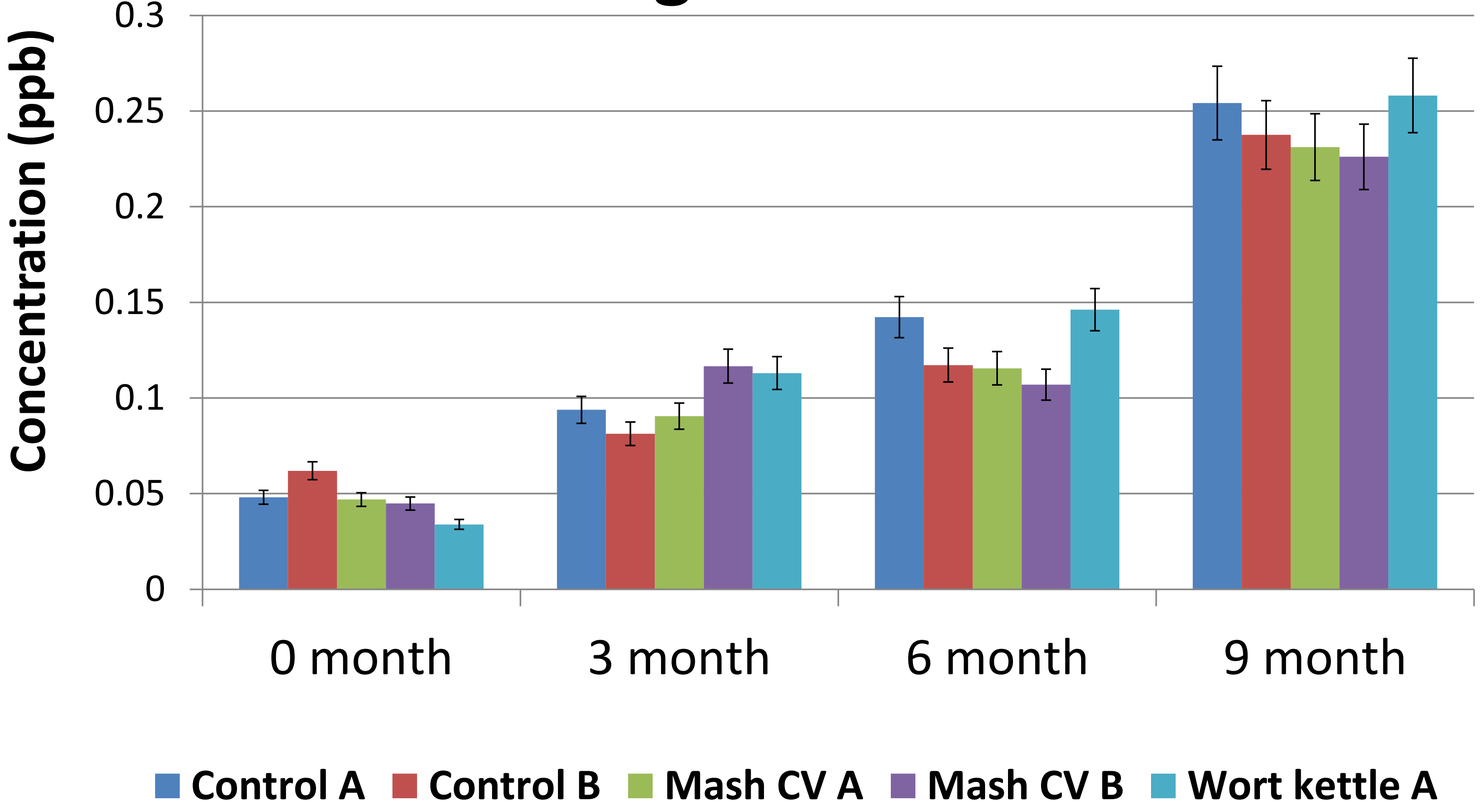
# Results – Large scale brewing trials
# Finished beer EPR area



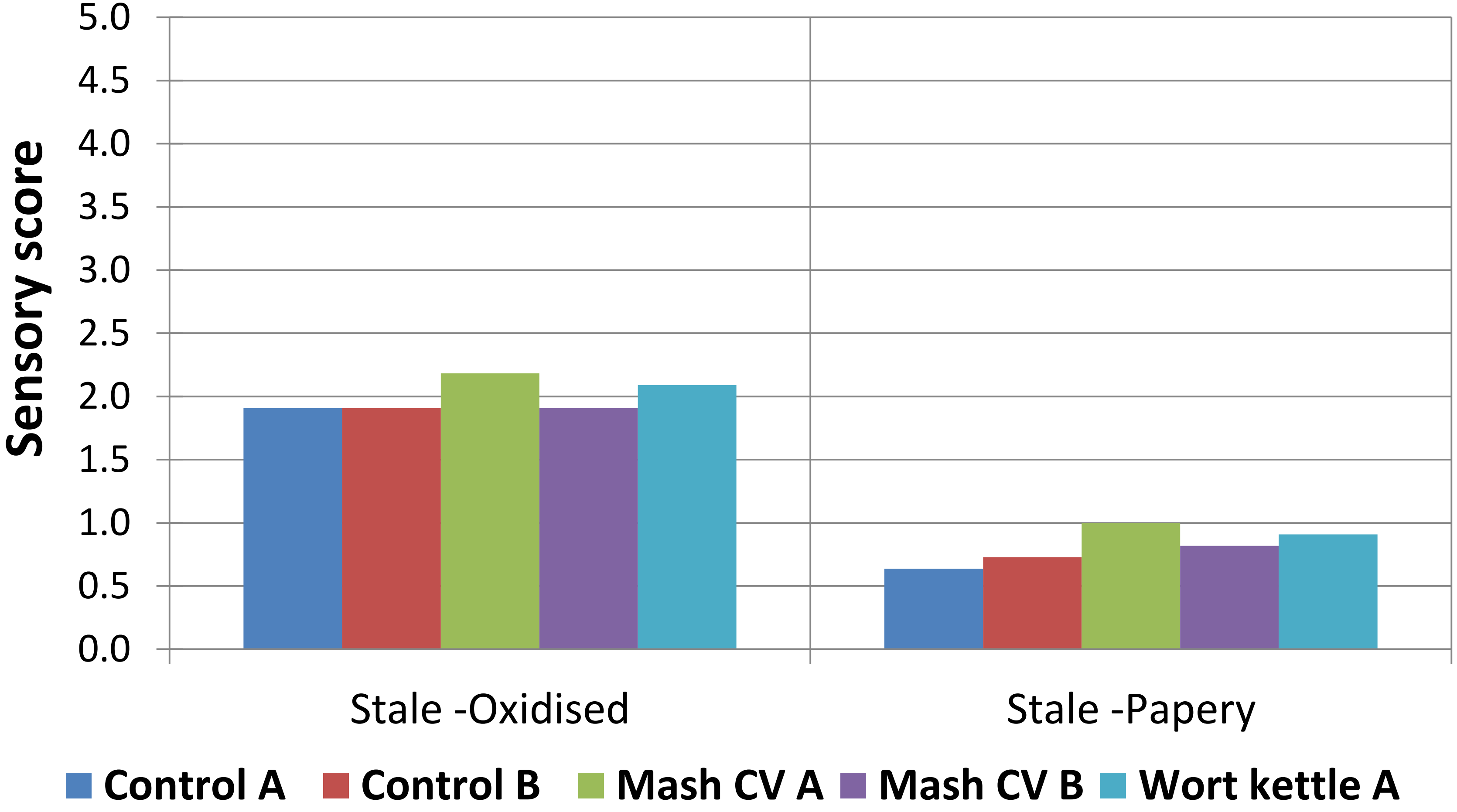
# Metal ion contents in fresh beer samples



# t-2-nonenal beer samples during storage at 20°C



# Sensory Analysis after 9 months storage at 20°C



# Summary
# Full-scale brewing trials

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- **No significant difference** between any of the trial conditions was observed for **t-2-nonenal or sensory analysis**
- **No significant effect** of the GT addition **on Fe-levels** in **finished beers**
- In general very low Fe-levels, good sensory scores and acceptable t-2-nonenal formation for all samples

# Summary
# Full-scale brewing trials

- EPR results indicated a higher radical formation rate in the kettle addition trial, but this didn't correlate with sensory staling or aldehyde data
- EPR results might have been influenced by other factors:
  - Wort kettle addition showed higher Mn-level and lower $SO_2$-level (3 mg/l fresh beer)
  - Control A had very low Fe-level and the highest $SO_2$-level (5 mg/l fresh beer)

# Conclusions

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- **Clear benefits** of GT addition were observed **in the brewhouse** for both addition points:
  - Chelation of, and complex formation with, Fe-ions
  - Scavenging of radicals
  - Lower TBI
- **No clear evidence** of any impact of GT addition on the **flavour stability of finished beer**
- **Complimentary indices for flavour stability are required to understand and predict beer staling**

# Acknowledgments

- MolsonCoors UK
- University of Nottingham

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- Rod White
- Jonathan McMaster

At MillerCoors:

- Bob Foster
- Roman Ortiz

# Thank you for your attention!

ASBC

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# Control strong wort EPR spectrum after 200 min using a high-sensitivity cavity showing additional unknown peaks