Effect of Potassium Permanganate on the Biodegradation of Weathered Crude Oil from Indiana Harbor Canal

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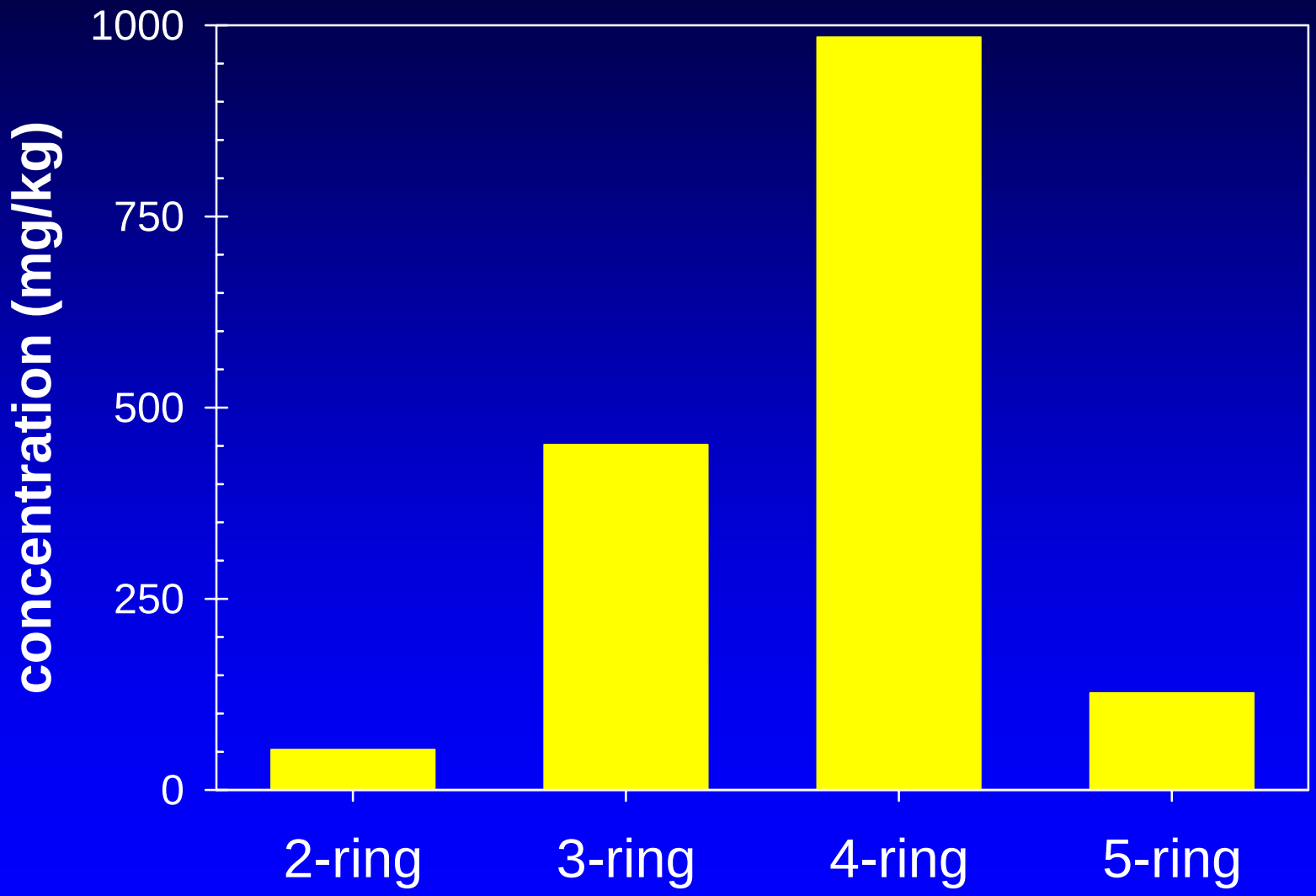
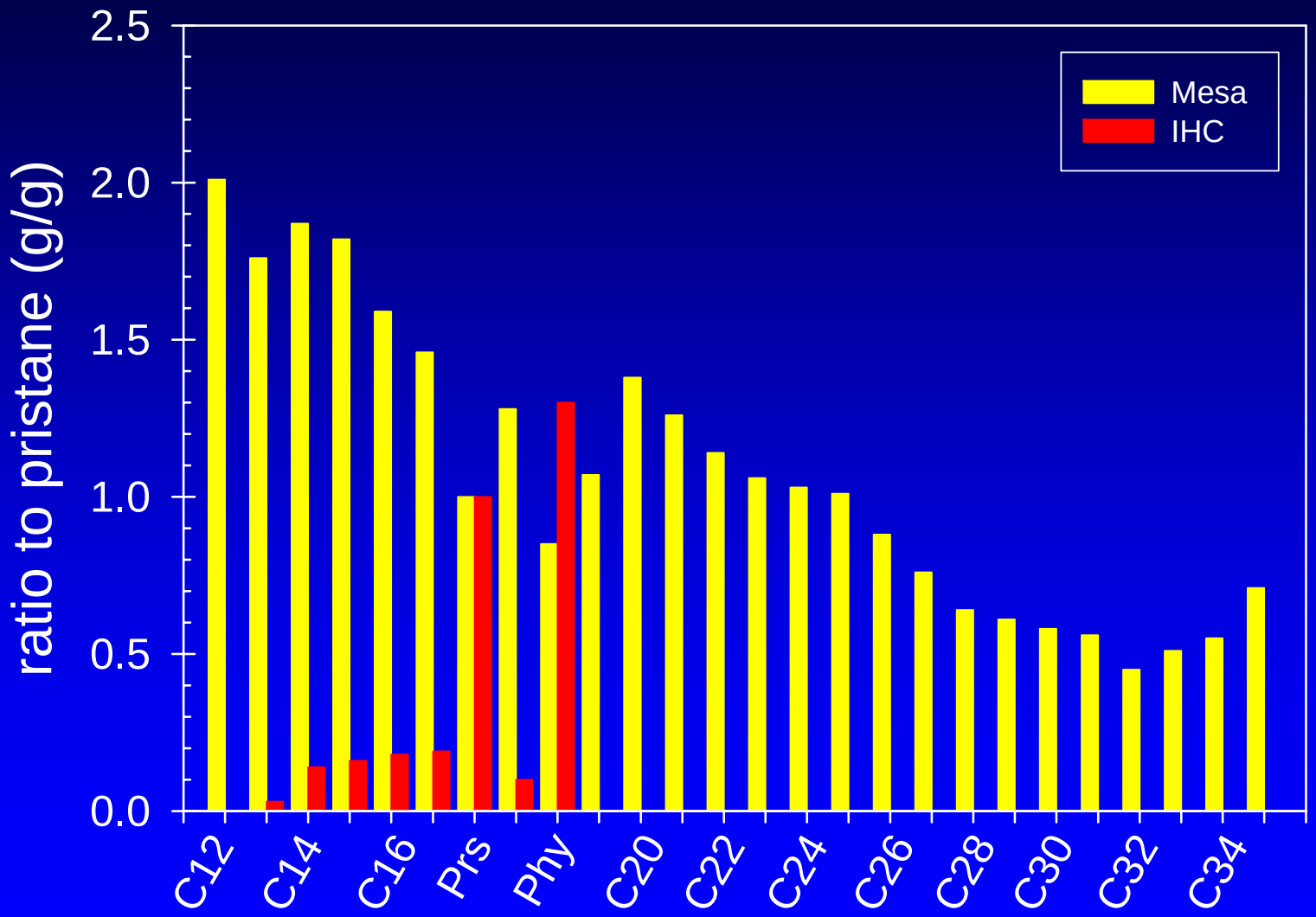
Indiana Harbor

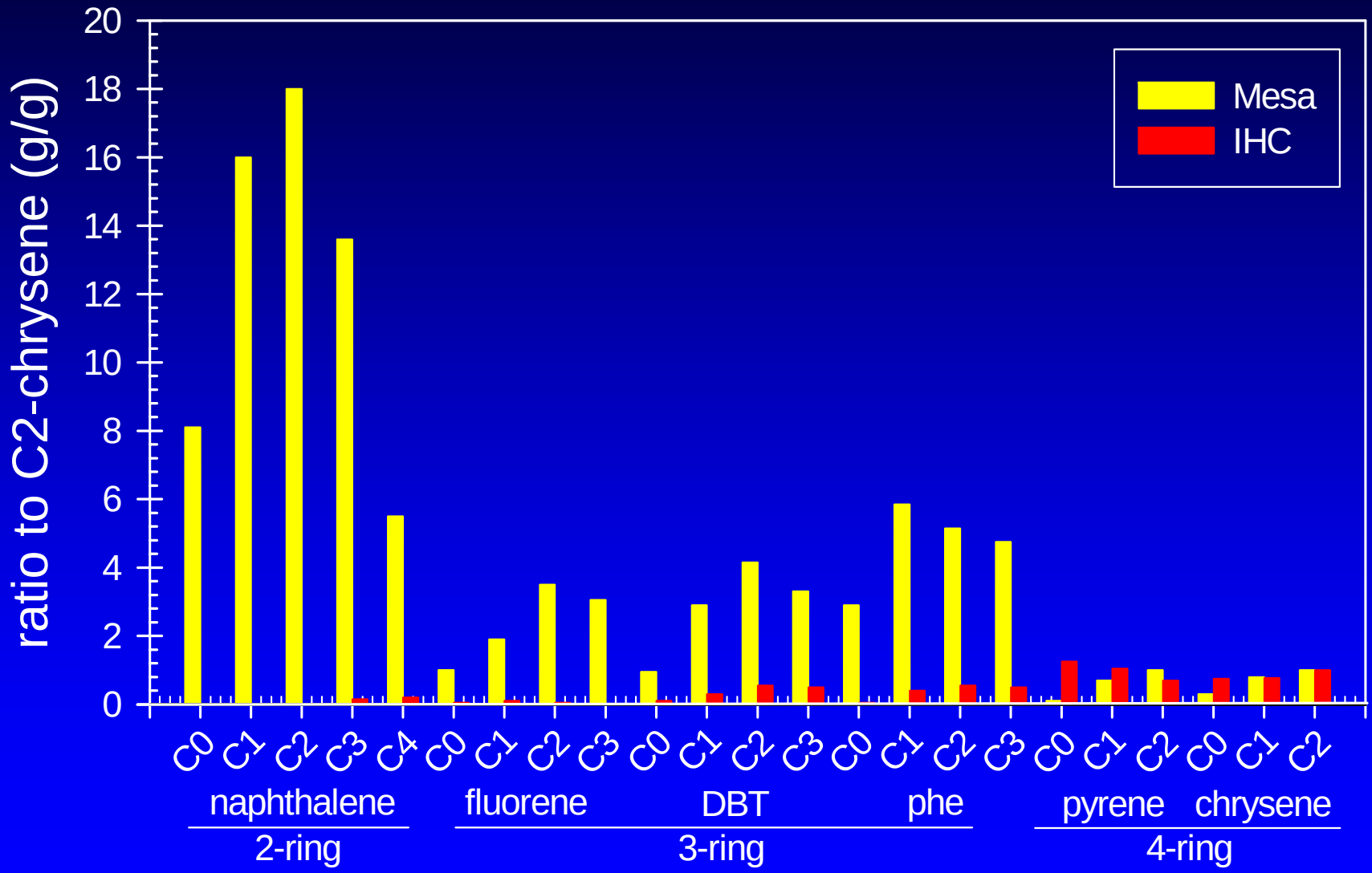
PAH Concentrations in IHC Sediments



Comparison of IHC Oil to Weathered Medium Crude Oil (Mesa): Alkanes



Comparison of IHC Oil to Weathered Medium Crude Oil (Mesa): Aromatics



Summary of Indiana Harbor Canal Shoreline Sediment Characteristics

- The IHC sediments are heavily contaminated
  - the sediments can be up to 40% oil by mass
- The IHC oil is highly weathered
  - the concentrations of easily degradable contaminants (e.g., normal alkanes and low MW PAHs) are very low relative to their more recalcitrant analogs (e.g., branched alkanes and alkyl-substituted high MW PAHs)
  - IHC oil contains high absolute concentrations of compounds of concern (e.g., 4- and 5-ring PAHs)

Proposed Method of Treatment:

Use chemical oxidation by potassium permanganate ($KMnO_4$) or hydrogen peroxide (H_2O_2) to increase the biodegradability and bioavailability of IHC contaminants

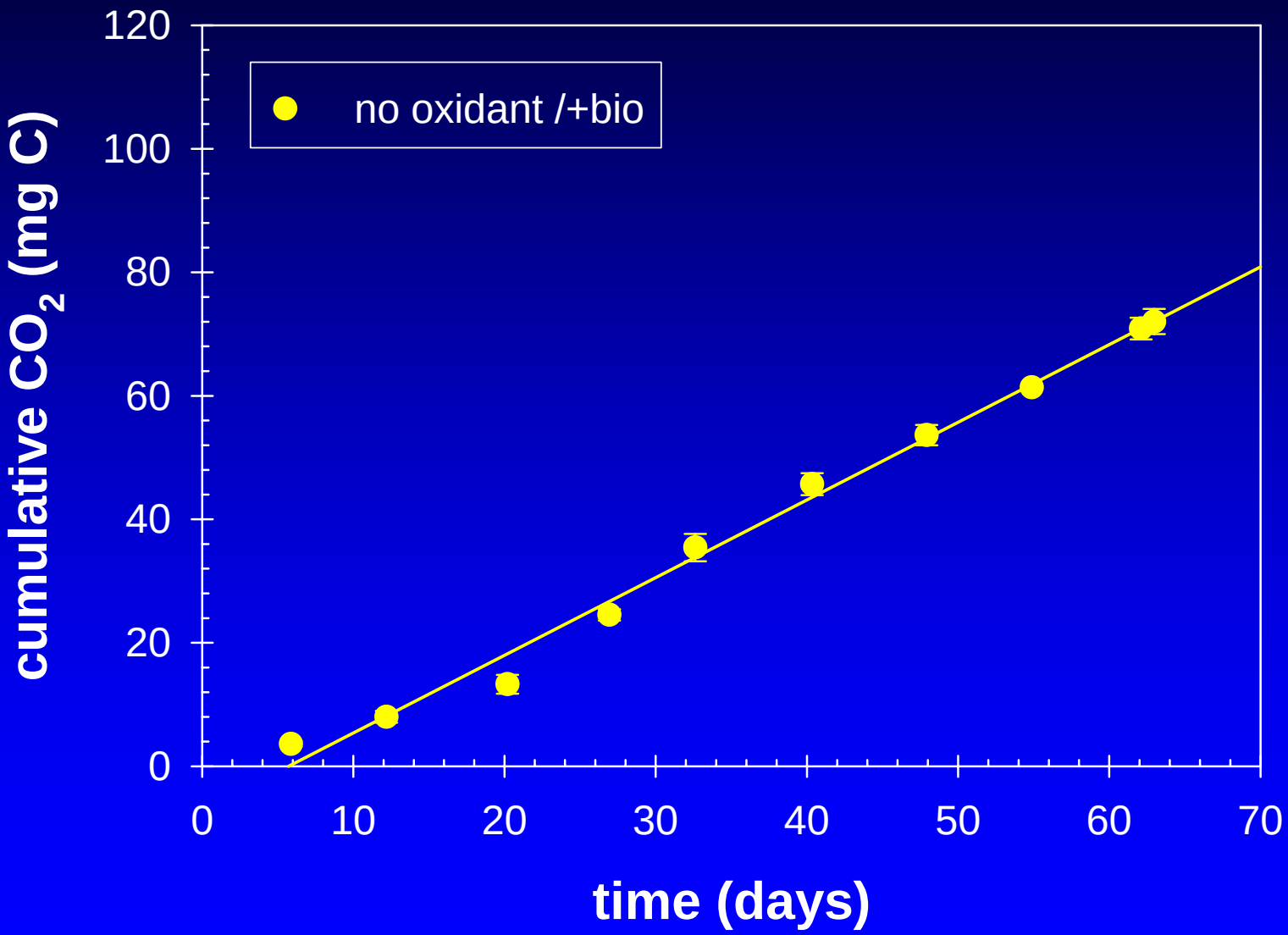
- 2.9 g H_2O_2/L
- 9.0 g $KMnO_4$/L

Proposed Mechanism:

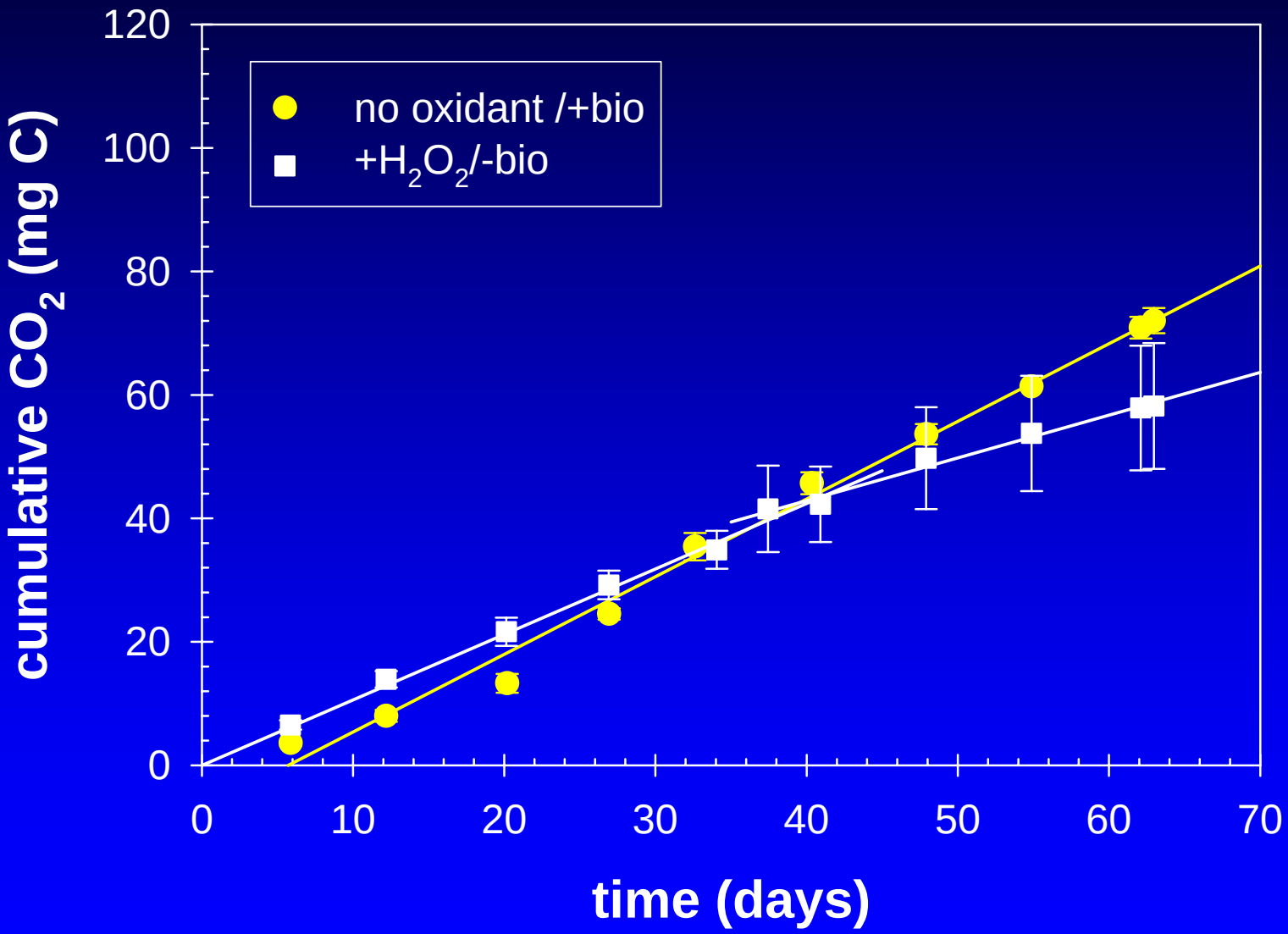
Oxidation will increase the bioavailability and biodegradability of contaminants by

- decreasing molecule size
- inserting hydrophilic functional groups

Oil Mineralization: No Oxidant Control



Oil Mineralization: $+H_2O_2$



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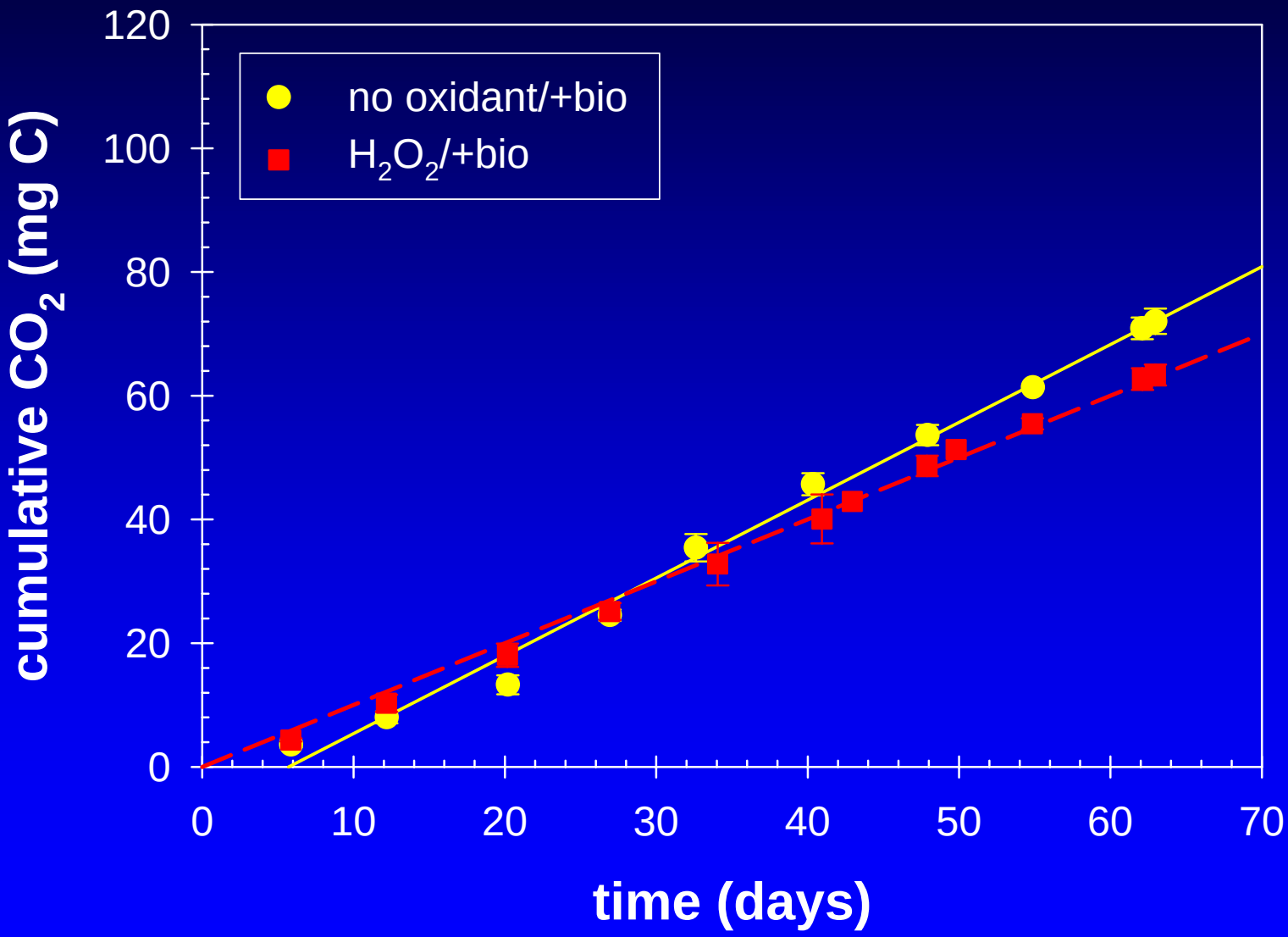
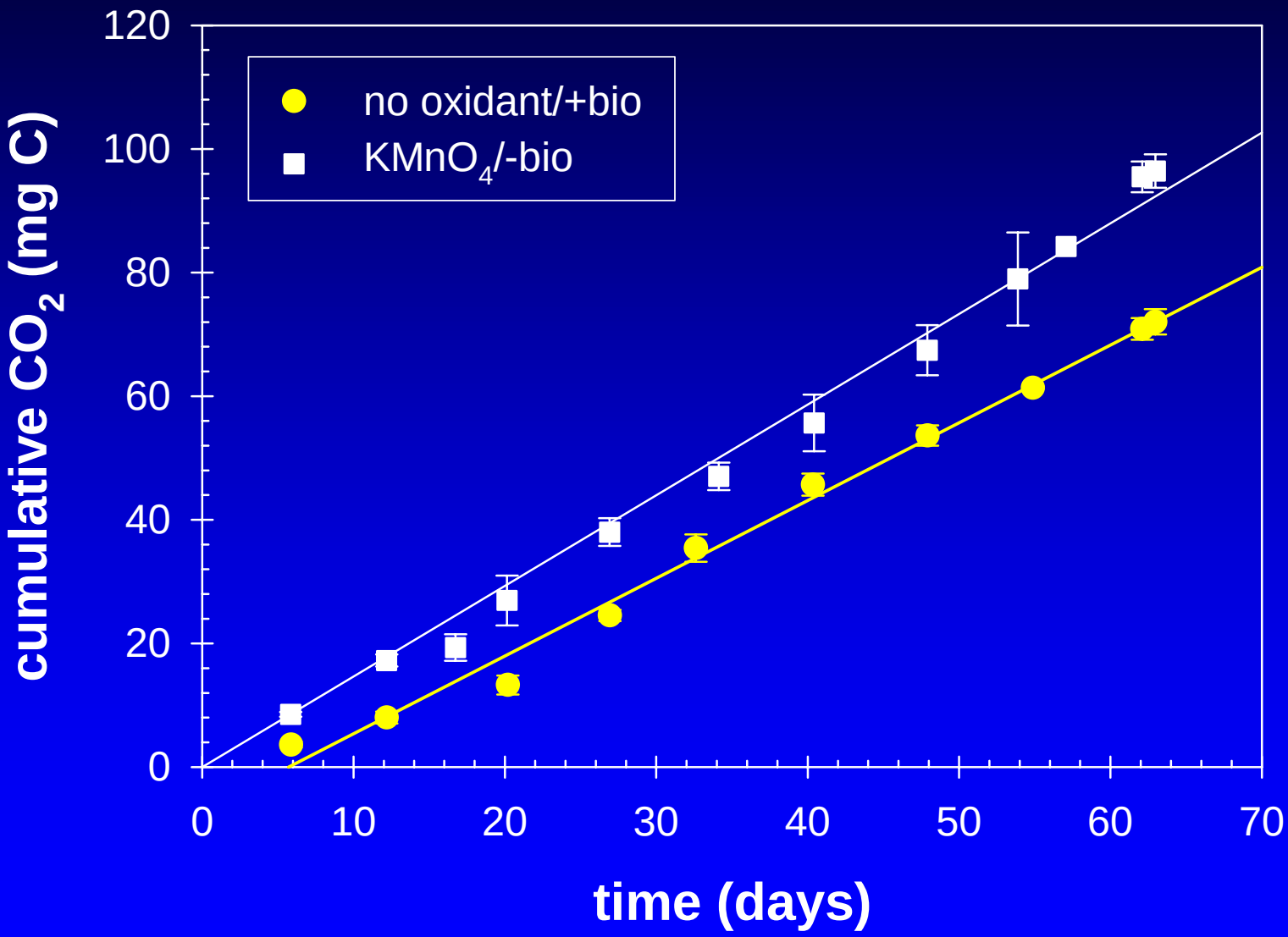
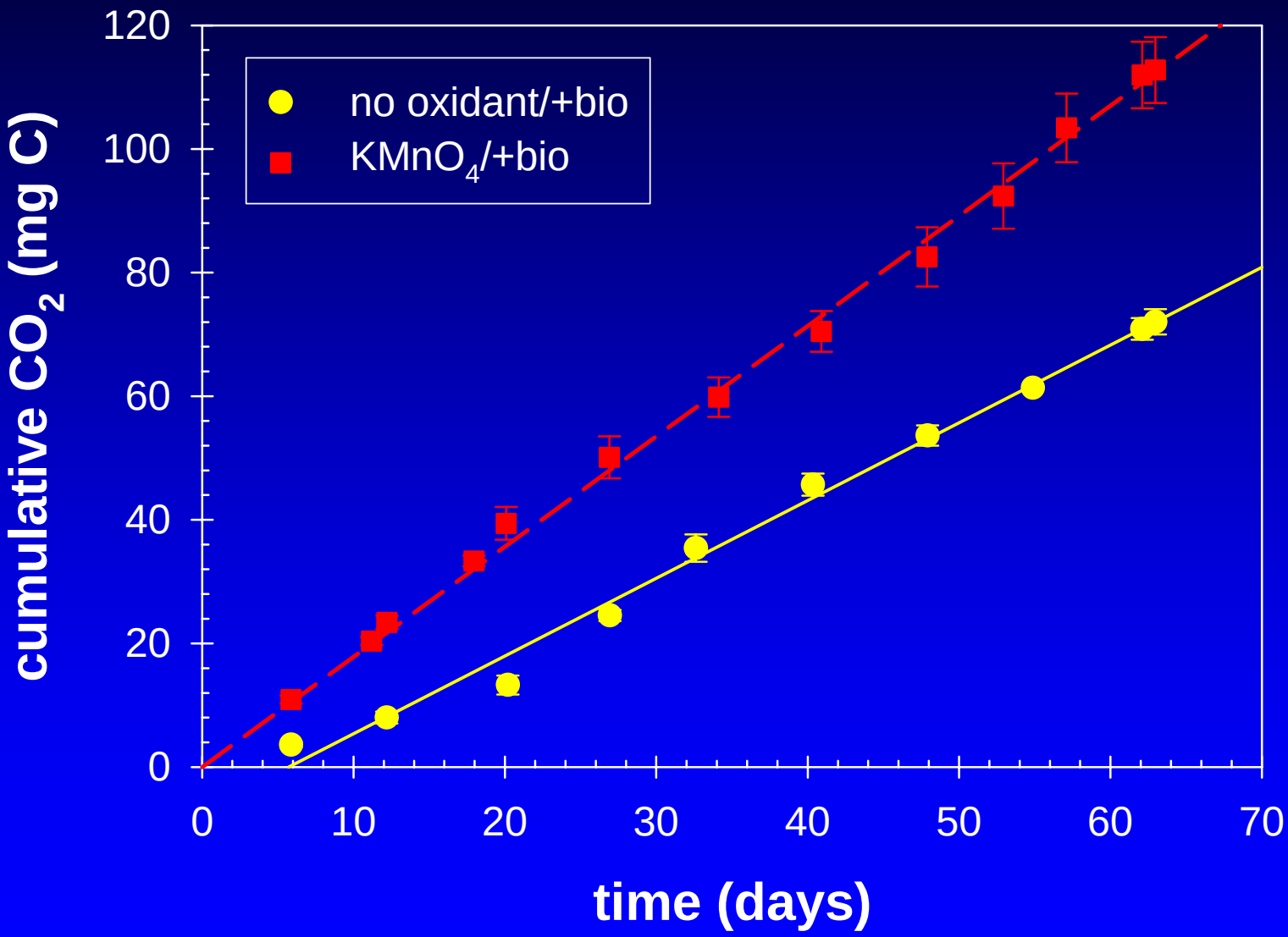


Oil Mineralization: +$KMnO_4$



Oil Mineralization: +$KMnO_4$



Summary of IHC Oil Biodegradation Experiments

∴ Permanganate is a more effective oxidant for the IHC oil than hydrogen peroxide

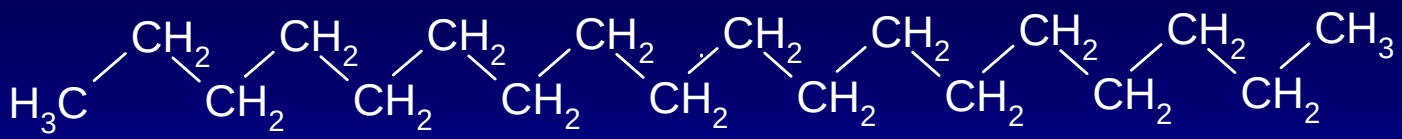
- effect of permanganate on components not measured by GC-MS is unknown

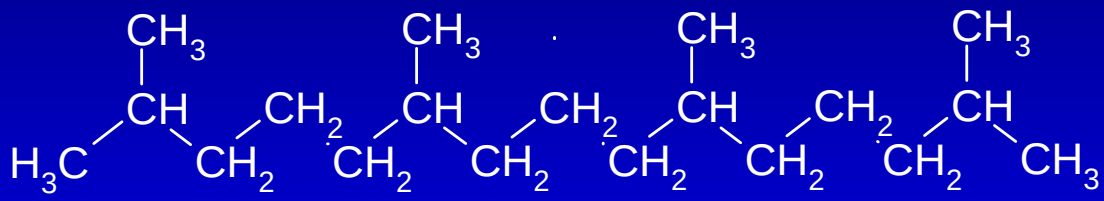
Next Step:

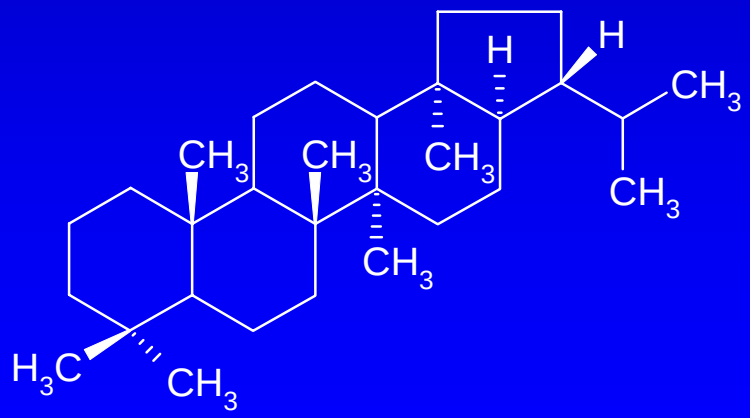
Determine effects of permanganate on the biodegradability of oil components with different chemical characteristics

- aliphatics, aromatics, resins, and asphaltenes

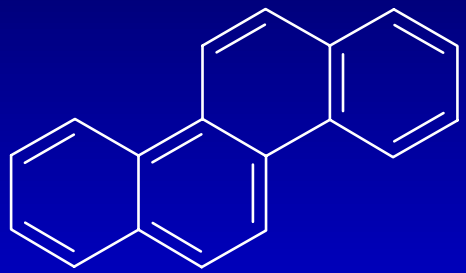
Aliphatic Hydrocarbons

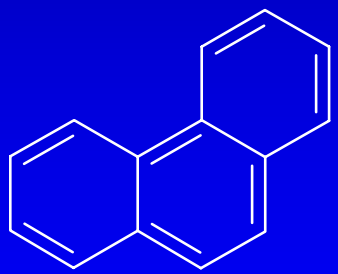


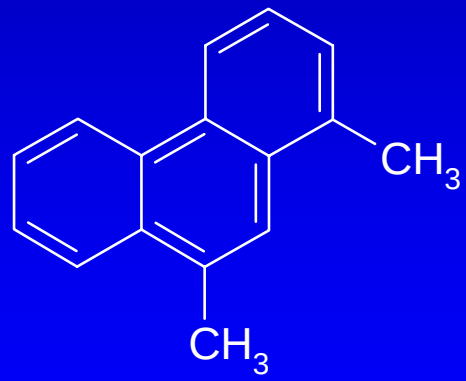




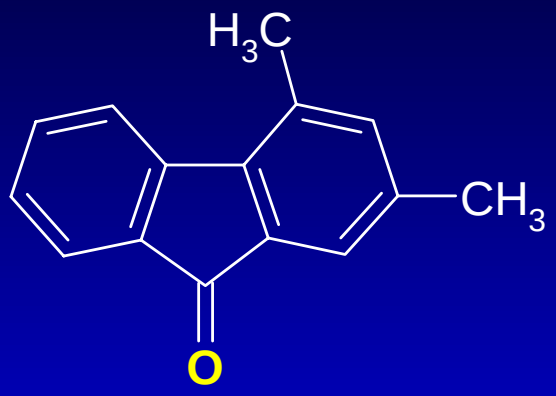
Aromatic Hydrocarbons

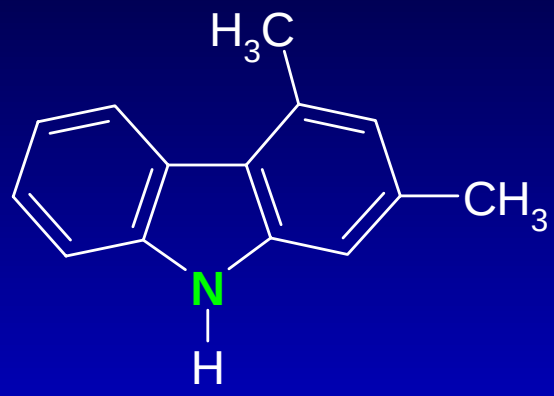


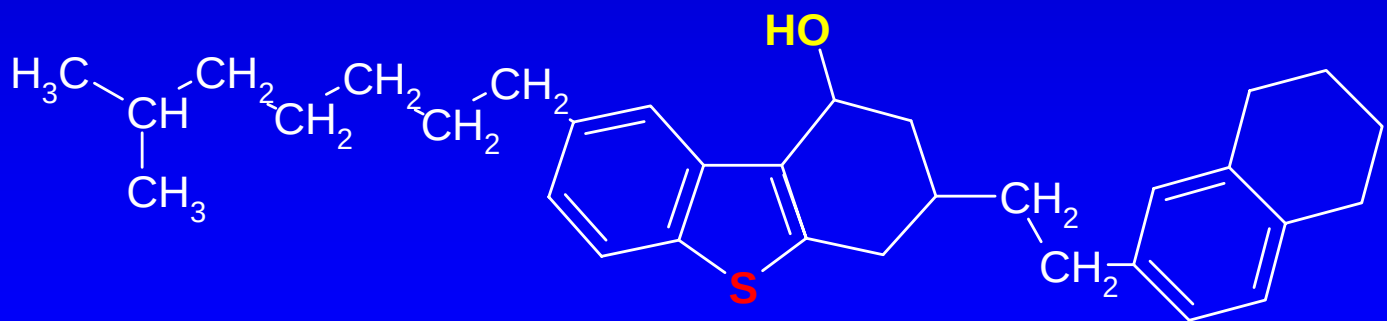




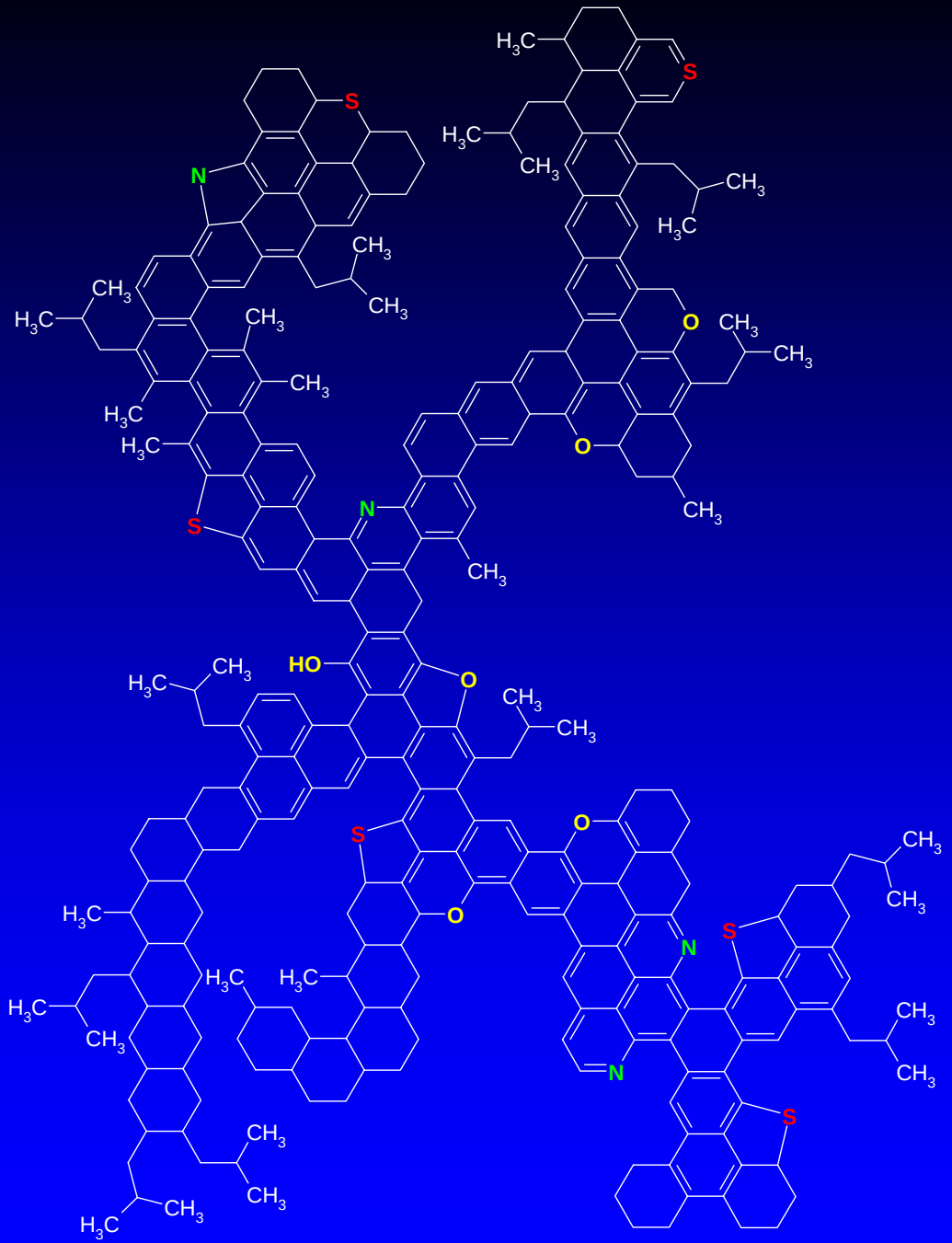
Resins



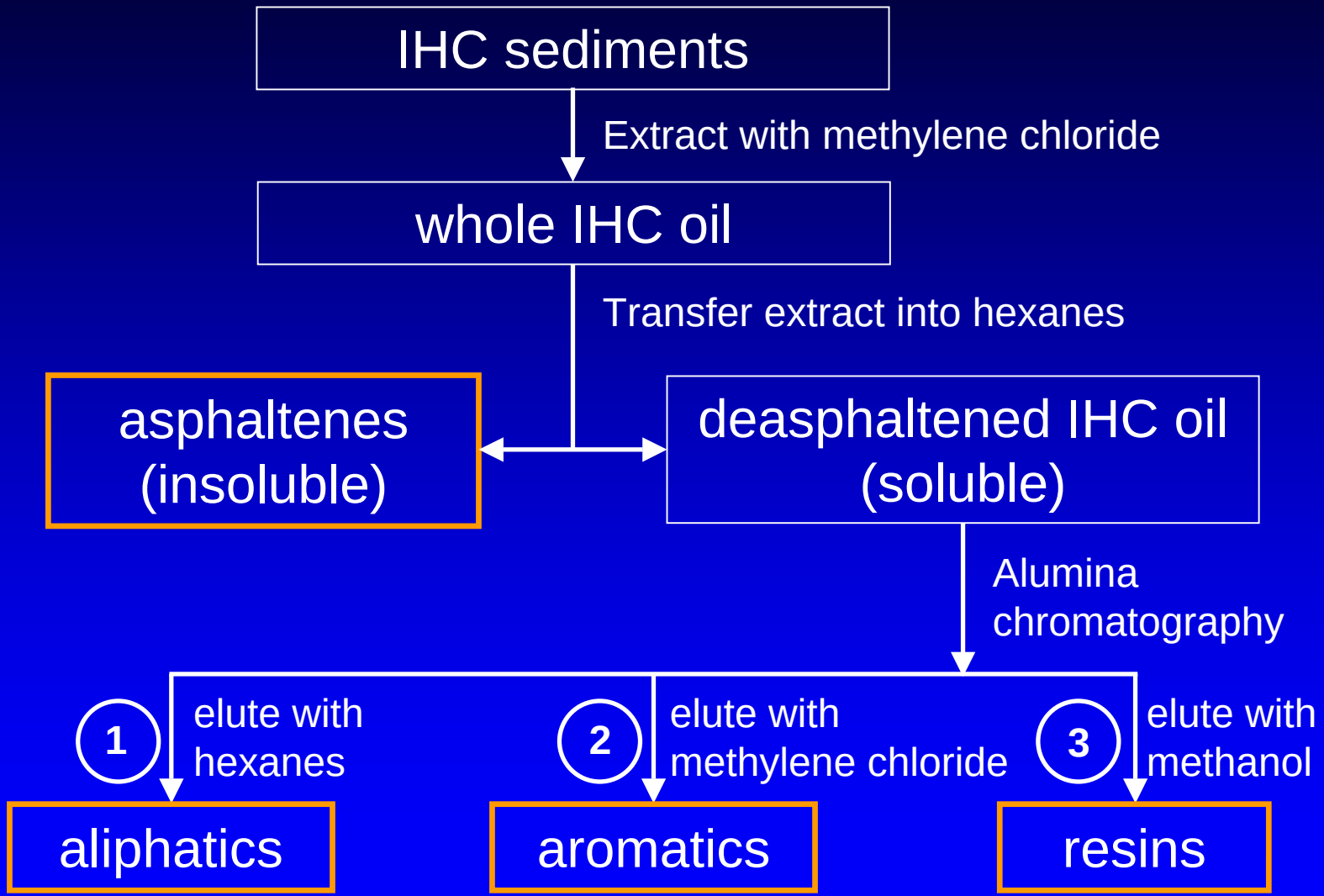




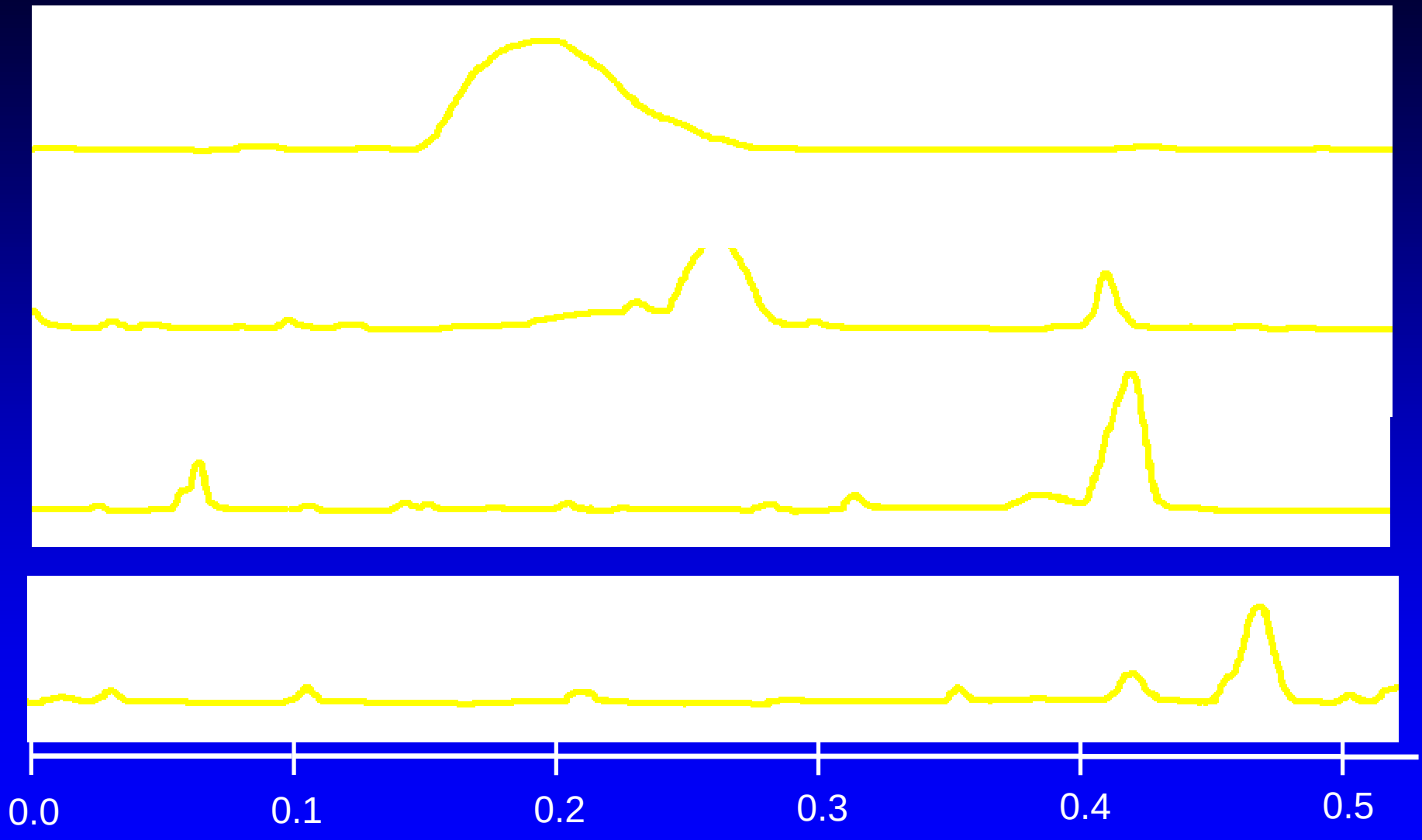
Asphaltenes



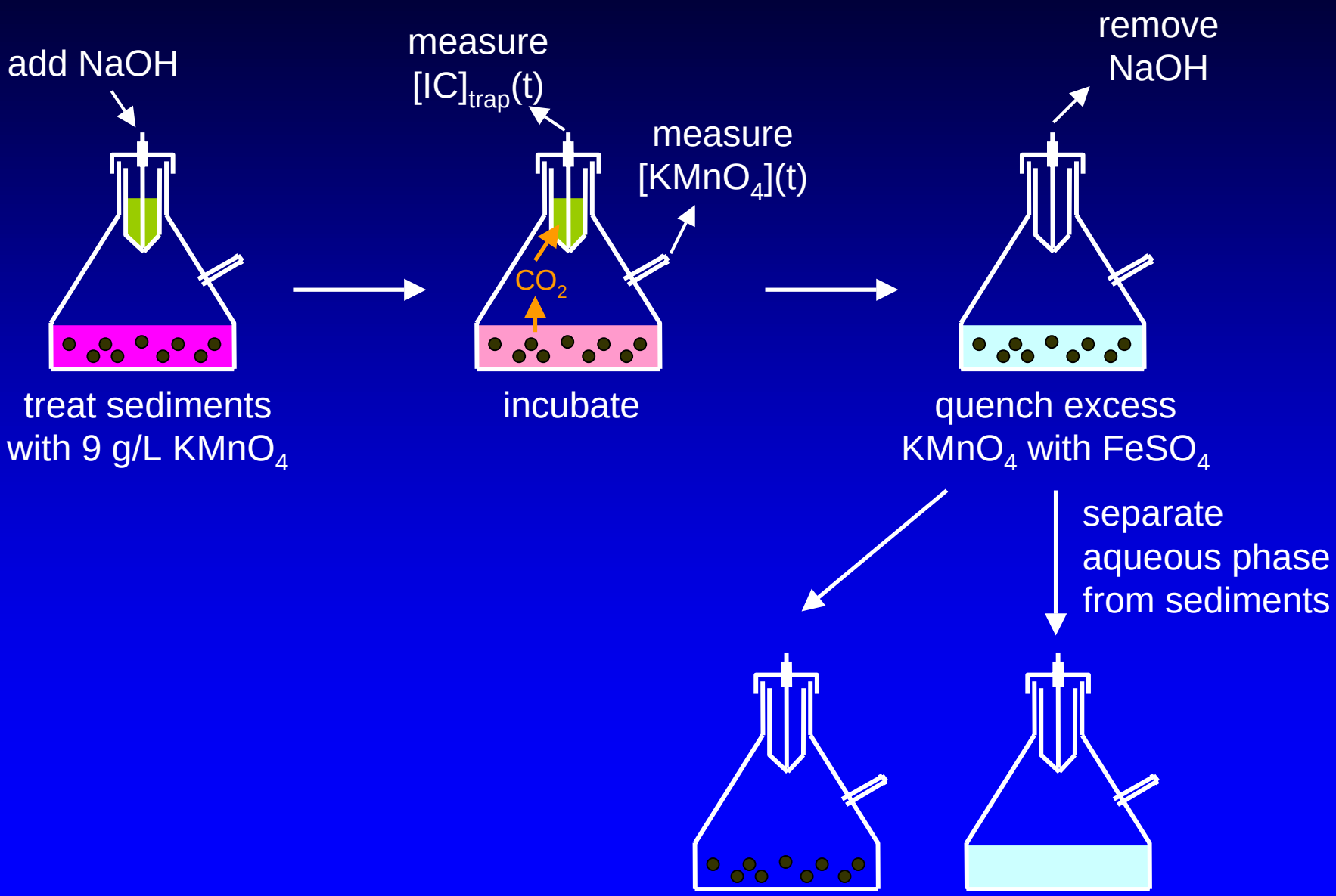
Separation of IHC Oil into Discrete Fractions



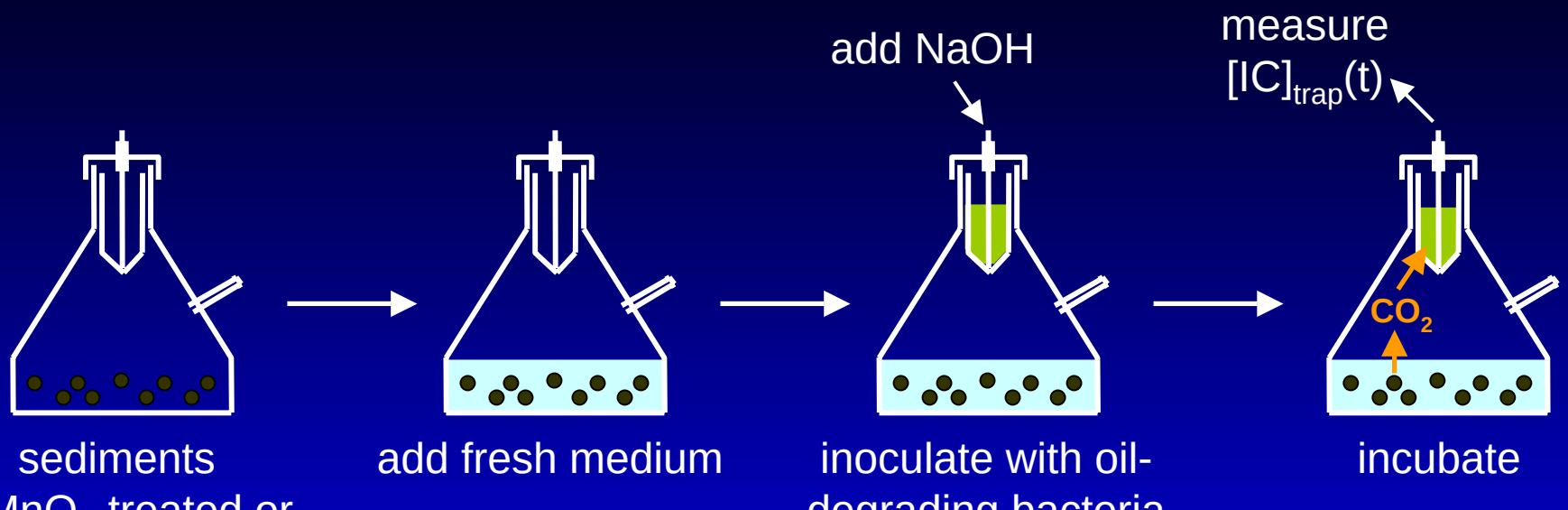
Iatroscan Analysis of IHC Oil Fractions

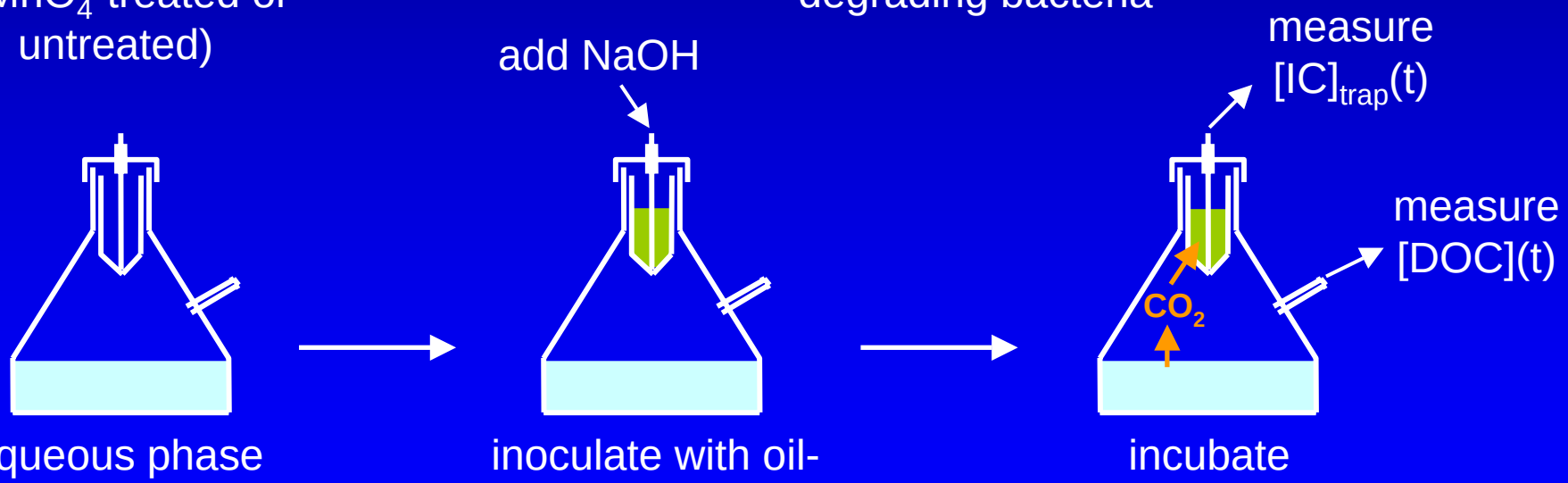


Experimental Approach: Chemical Oxidation

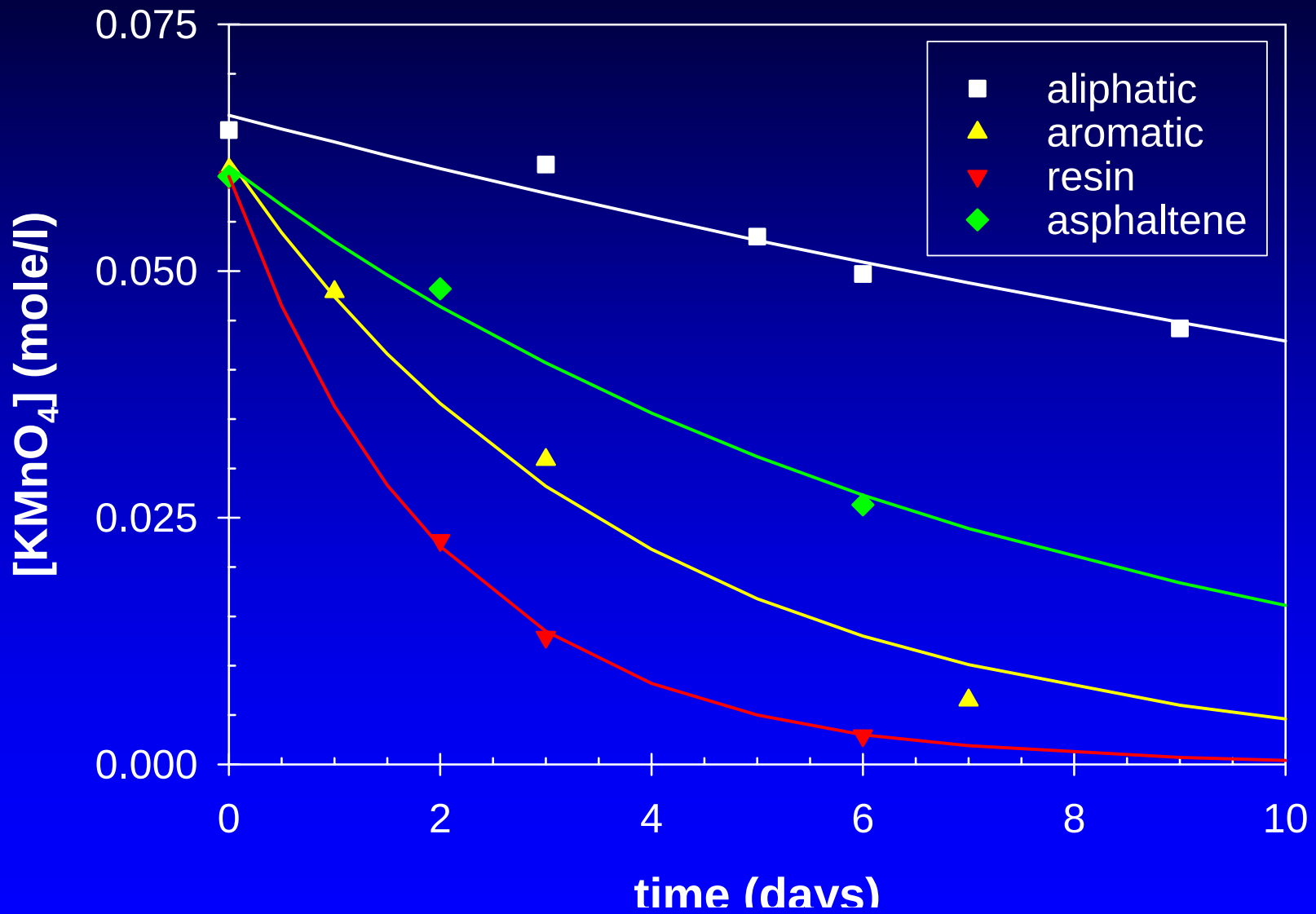


Experimental Approach: Biodegradation

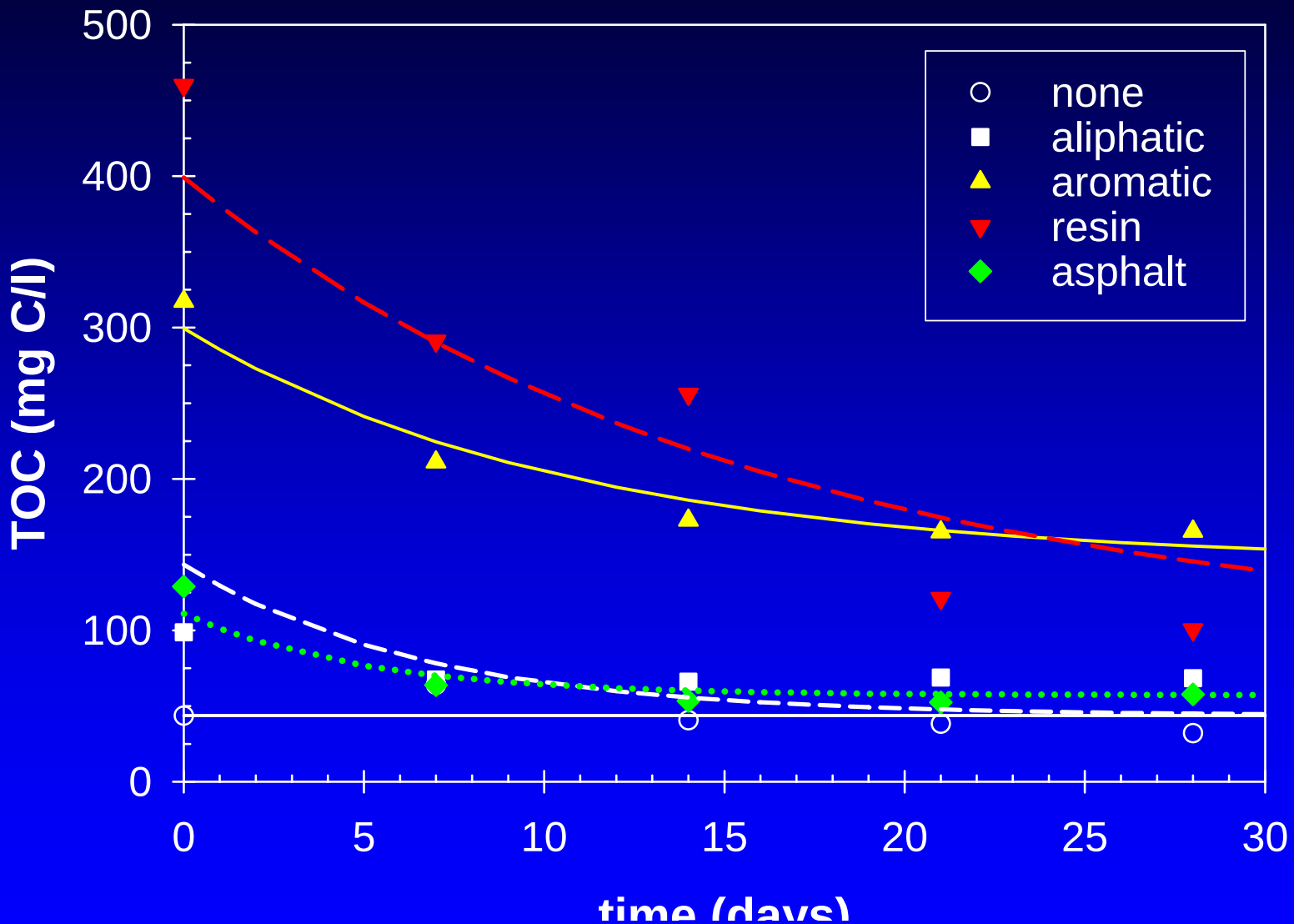




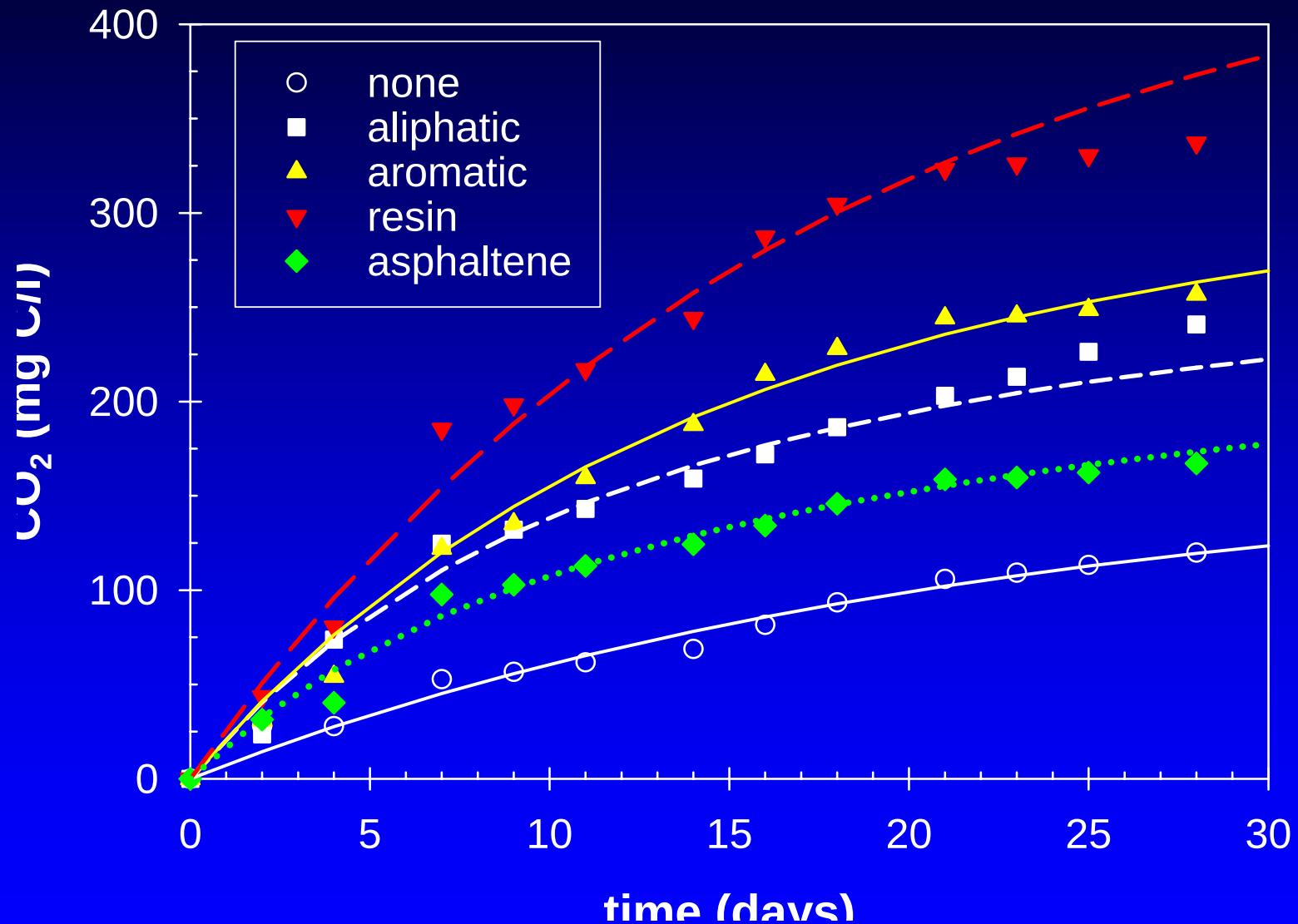
Reaction of Permanganate with IHC Oil Fractions



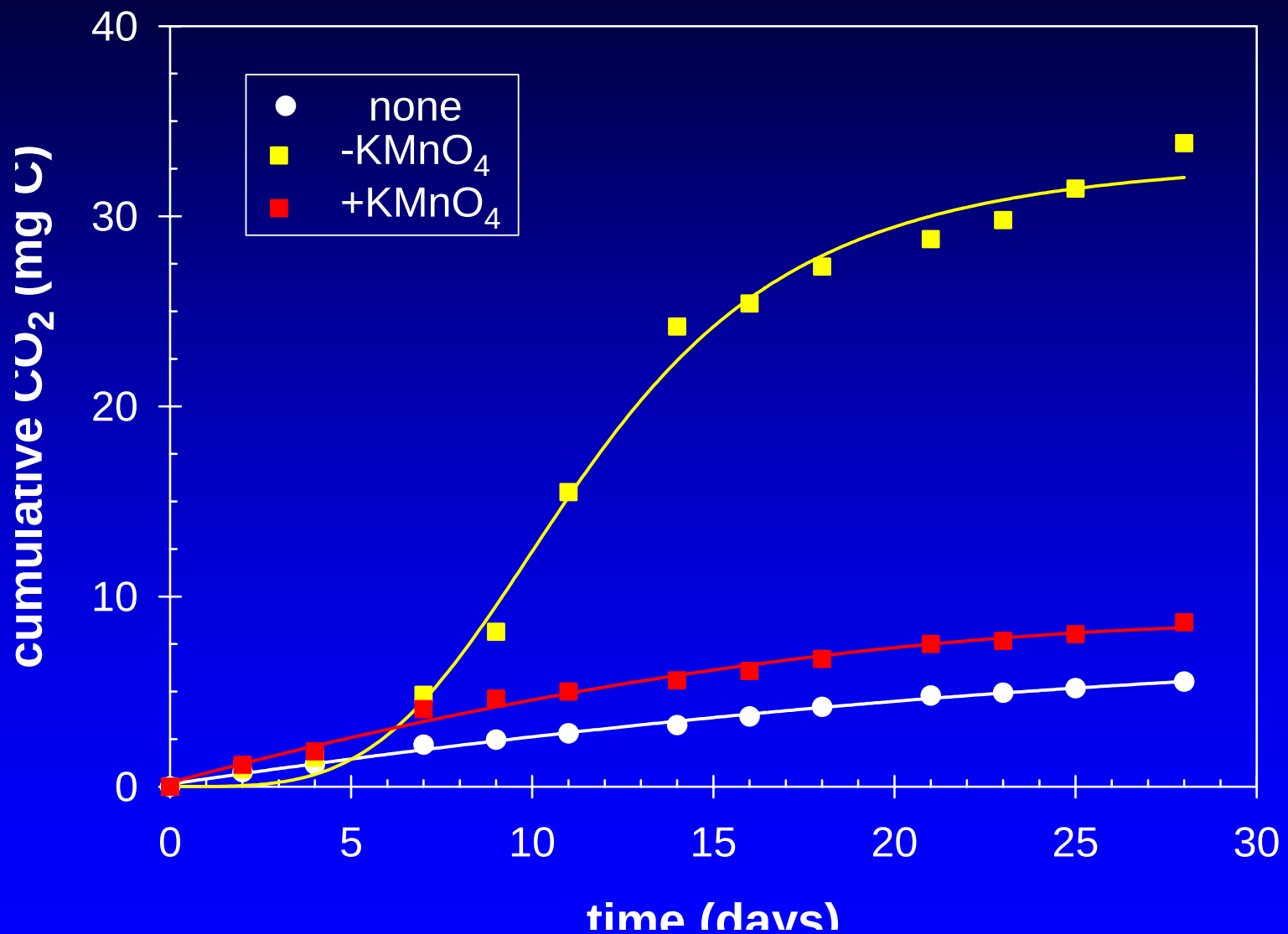
Biodegradation of Aqueous-Phase Products



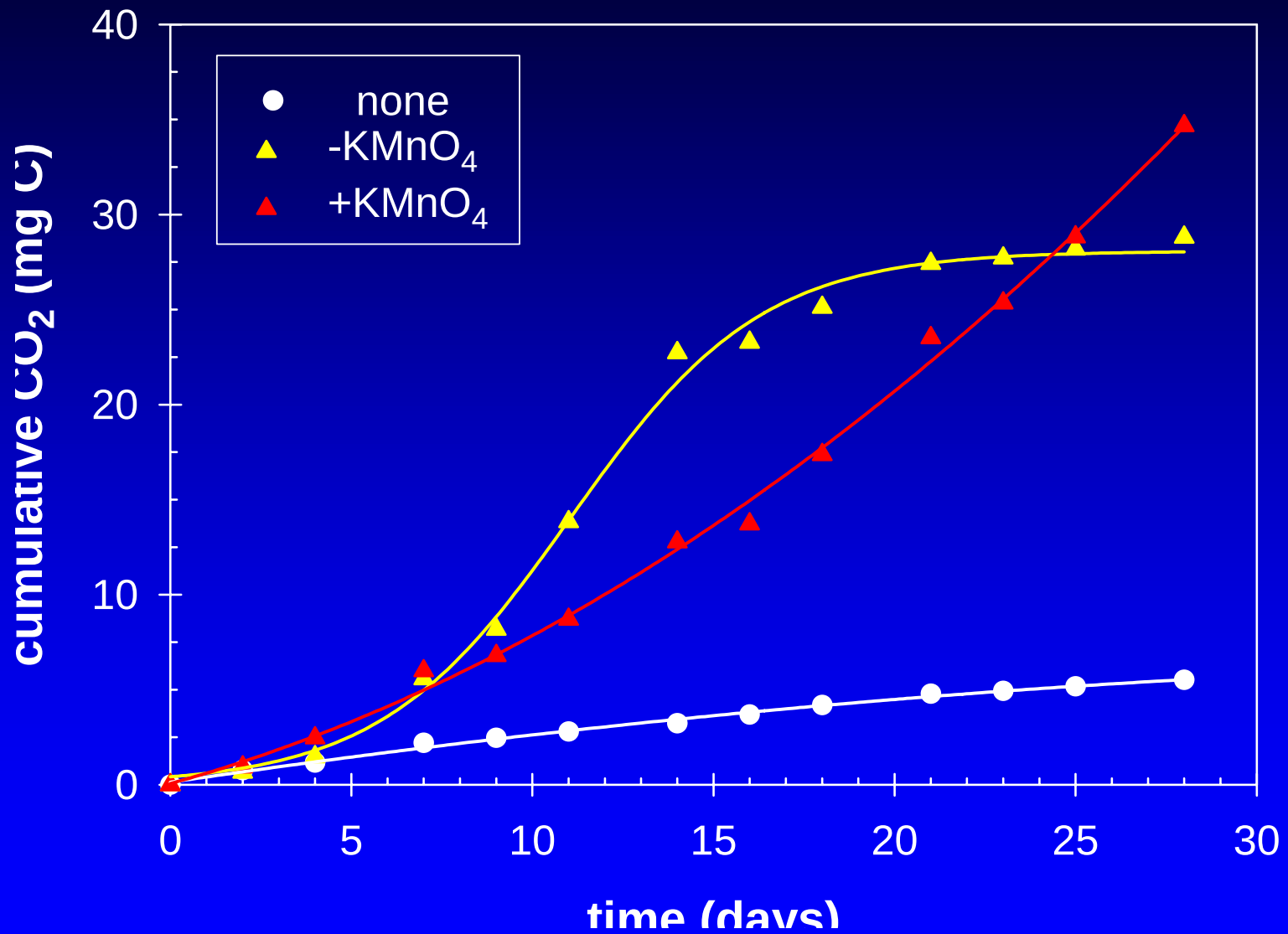
Mineralization of Aqueous-Phase Products



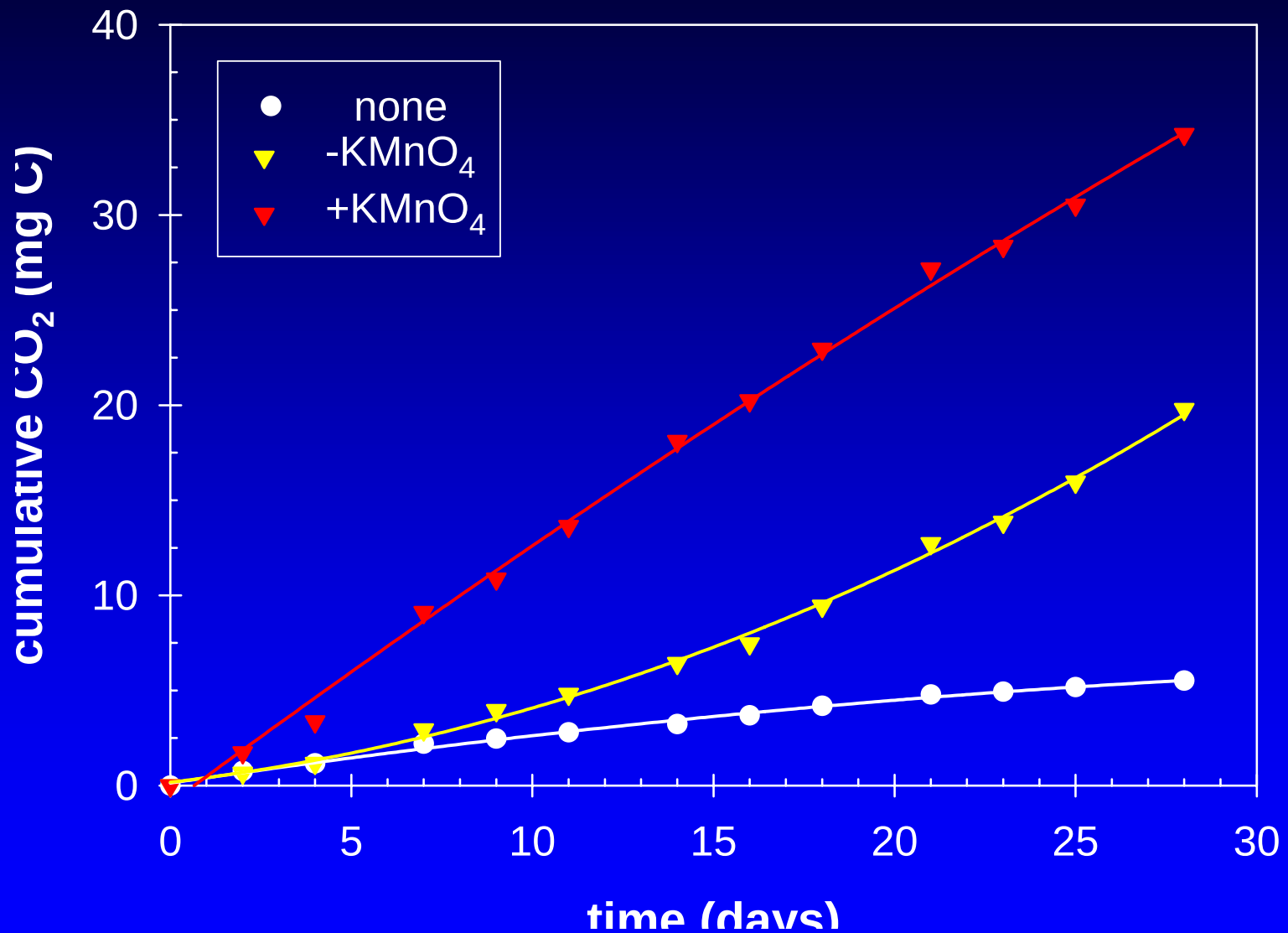
Biodegradation of Aliphatic Fraction



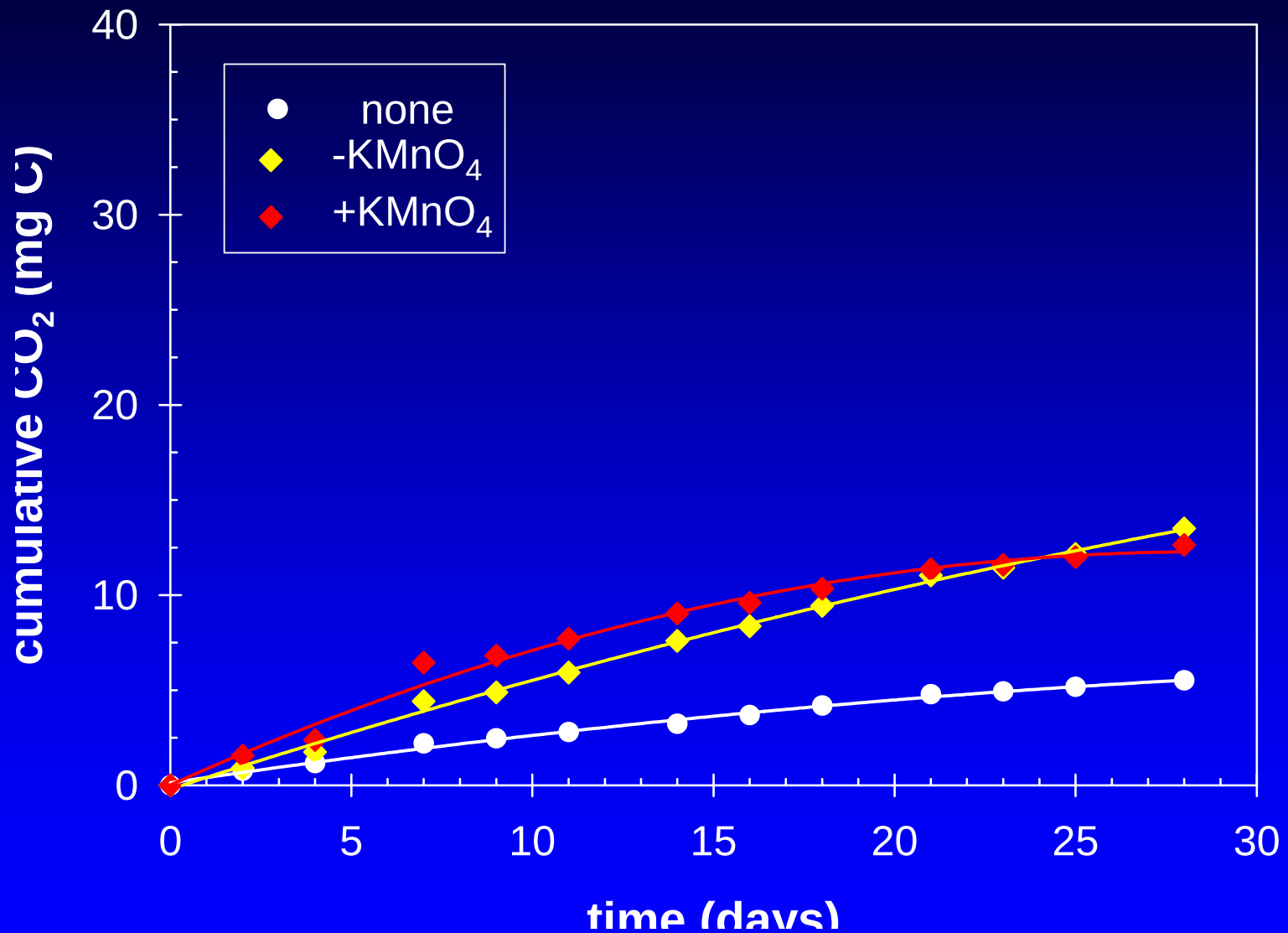
Biodegradation of Aromatic Fraction



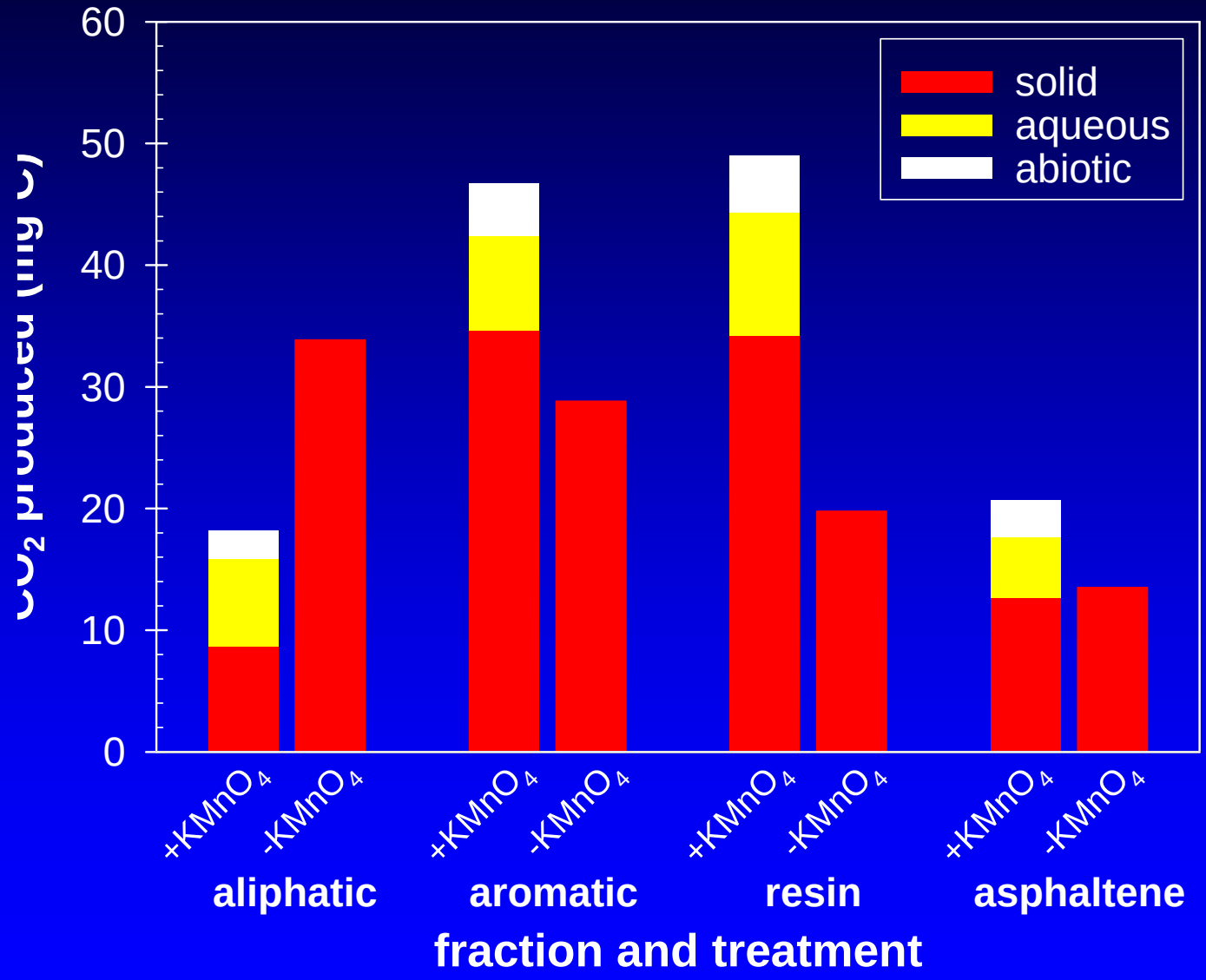
Biodegradation of Resin Fraction



Biodegradation of Asphaltene Fraction



Effect of Chemical Oxidation on Biodegradation of IHC Oil Fractions



Conclusions

- Permanganate reacted slowly with the aliphatic and asphaltene fractions
  - ➢ the solid-phase products were not more biodegradable than the parent compounds
    - treatment with permanganate reduced the biodegradability of the aliphatic fraction, probably by coating the oil-water interface with $MnO_{2(s)}$
  - ➢ very low concentrations of water-soluble products were formed
- Permanganate reacted quickly with the aromatic and resin fractions
  - ➢ the solid-phase products were more biodegradable than the parent compounds
  - ➢ the water-soluble products that were formed were easily biodegradable

Acknowledgements

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