Determination of the peroxide value in algae oil by ^{19}F-NMR – method comparison

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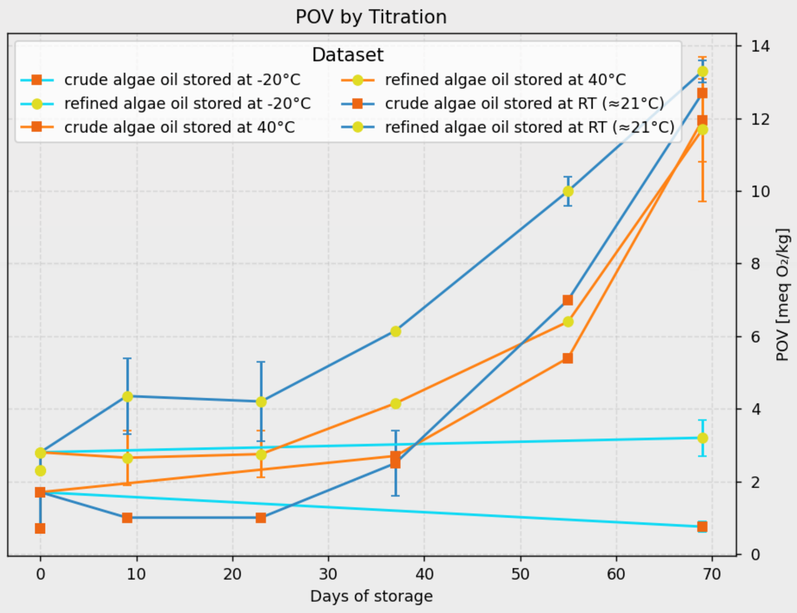

Fig. 1: Results of POV determination by classic Wheeler titration in algae oil

The peroxide value (POV) is typically determined by nonspecific Wheeler titration. Nuclear magnetic resonance (NMR) spectroscopy already enables direct quantification of hydroperoxides and calculation of POV in a single ^{1}H-NMR experiment (Fig 4). An even more efficient and sensitive alternative based on ^{19}F-NMR is presented (Fig. 5 + Fig. 6). This method measures oxidative capacity in lipid matrices (oils, fats, lecithin, krill oil) not covered by the other methods. The Algae oil analysed in this study is known to be a challenging matrix for POV determination. Interpretability of titration results in the algae oil is limited (Fig. 1), calling for a different method better suited for the matrix. The aim was to validate if the ^{19}F-NMR method is viable alternative for quality control.

^{19}F-NMR titration with TTFMPP

- Redox reaction of 4-,5-Bis-Trifluoromethylphenylphosphine (TTFMPP) with Hydroperoxides
- Formation of 4-,5- Bis-Trifluoromethylphenylphosphine oxide (TTFMPPO) (See Fig. 2)

- Several small Signals of different hydroperoxide species in ^{1}H-NMR
- One intense signal in ^{19}F-NMR → Sensitive ^{19}F-NMR determination
- 200 mg of sample, 5min of preparation, 10h of reaction time (Fig. 3)

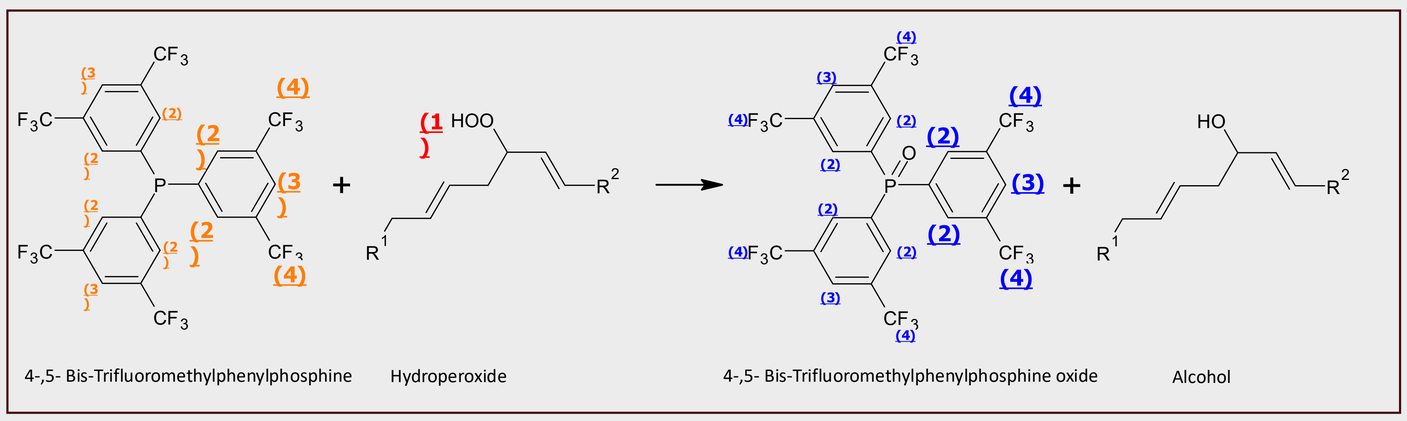

Fig. 2: Reaction of TTFMPP and Hydroperoxide to TTFMPPO and Alcohol

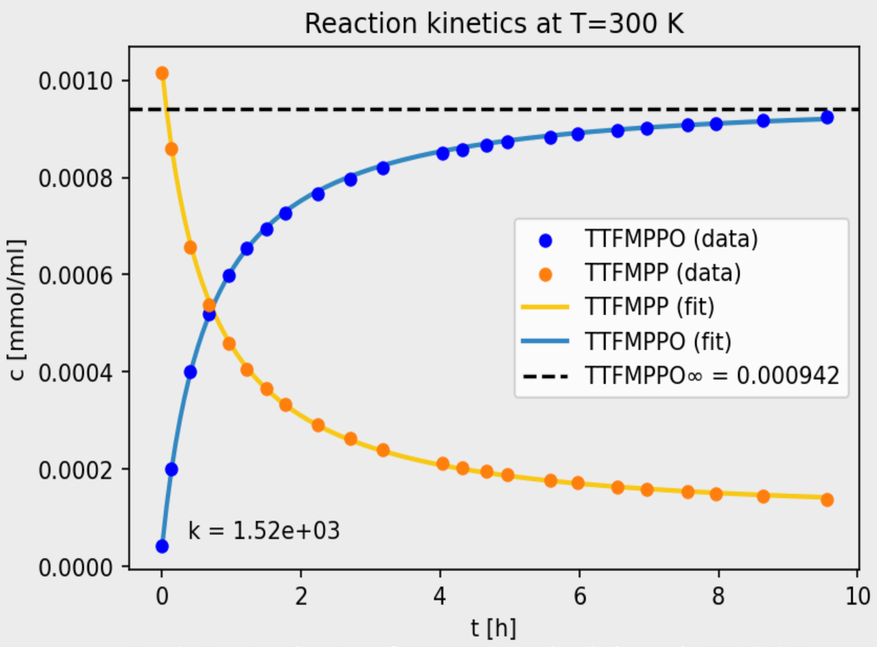

Fig. 3: Reaction kinetics of TTFMPP in oxidized algae oil at T=300 K. Second order kinetics fit

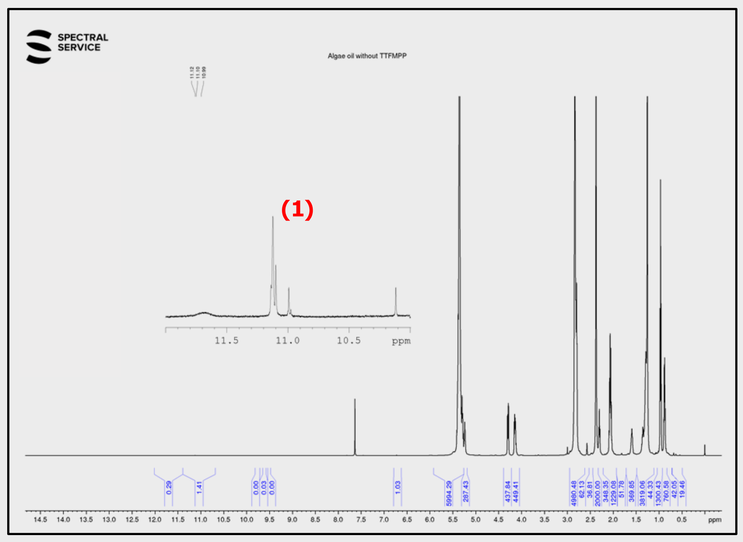

Fig. 4: ^{1}H NMR spectrum of algae oil – zoom on peroxide region

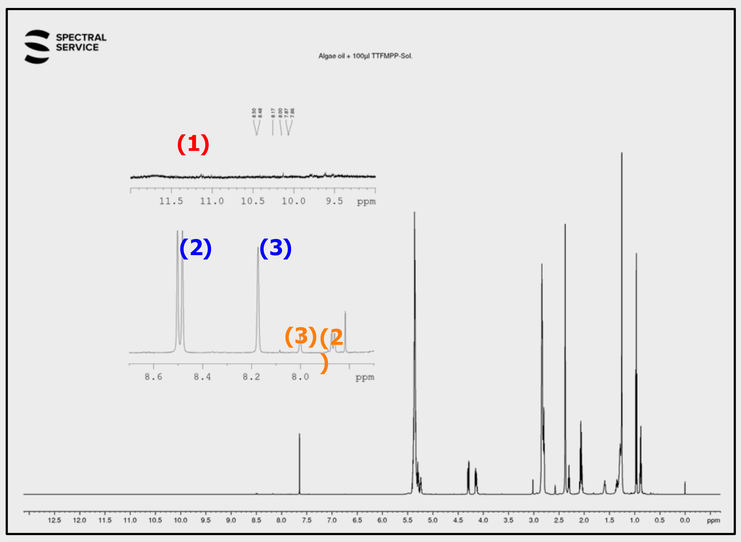

Fig. 5: ^{1}H NMR spectrum of algae oil after addition of TTFMPP

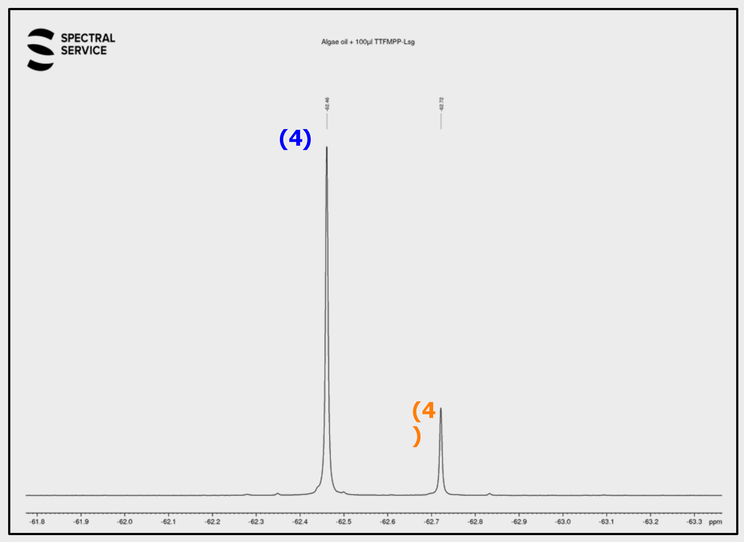

Fig. 6: ^{19}F NMR spectrum of TTFMPP + TTFMPPO in algae oil

Method Comparison

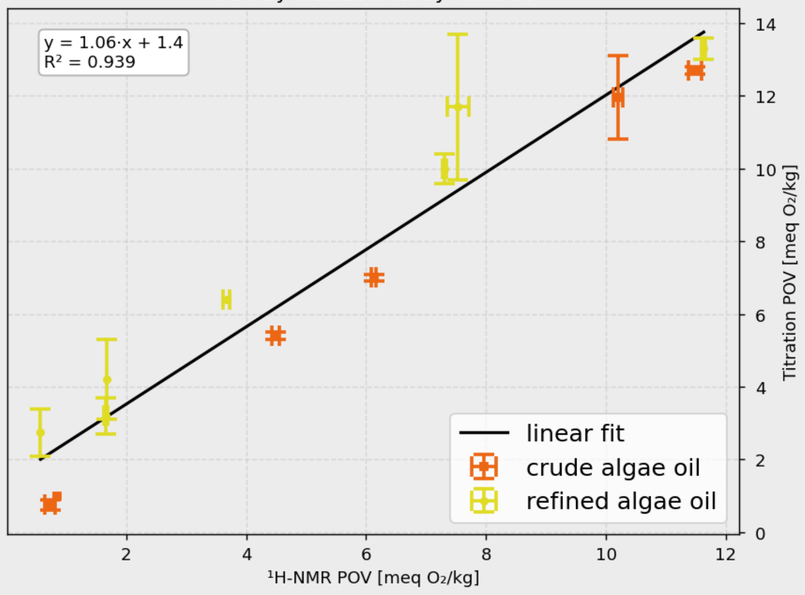

Fig. 7: Comparison of POV determined by Wheeler titration and ^{1}H NMR

- Offset of crude algae oil vs. refined algae oil for both titration methods
- Possible influence of other redoxactive compounds on titration
- ^{19}F-NMR titration results more robust to differences between crude/refined algae oil
  - More specific than Wheeler titration
- Smaller error of ^{19}F-NMR titration than Wheeler titration

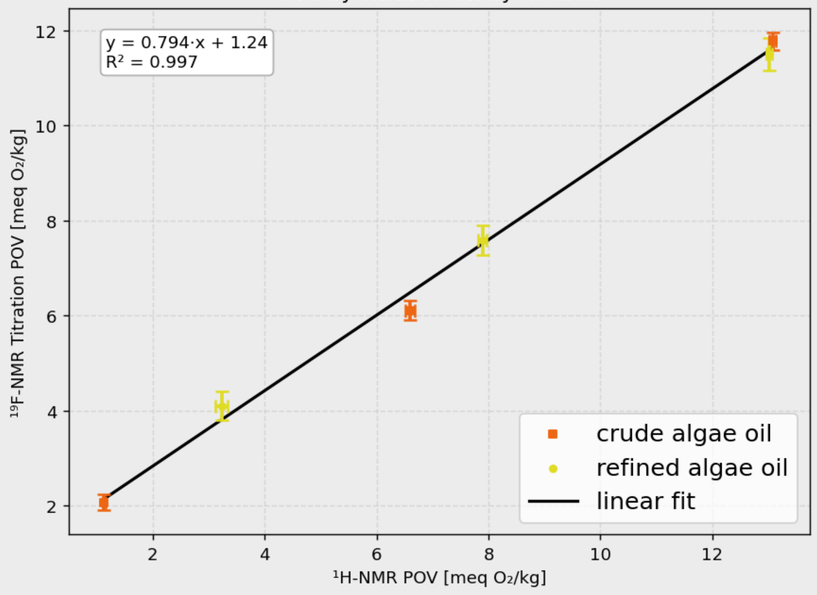

Fig. 8: Comparison of POV determined by ^{19}F-NMR titration and ^{1}H NMR

While both NMR methods can be used on as little as 200 mg of lipid sample, the ^{19}F-NMR method offers additional sensitivity. The results suggest that the ^{19}F-NMR method is more specific and precise than the classic Wheeler titration. In conclusion, the ^{19}F-NMR method for determining the POV has proven to be a viable method for quality control on algae oil.

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