



Determination of peroxide value in microalgae oil by ^{19}F -NMR

Method comparison

Why NMR, why this topic?

Analysing the peroxide value (PV) in the provided Microalgae oil is challenging. PV is typically determined by nonspecific titration. Interpretability of early titration results in the algae oil is limited (Fig. 1), calling for a different method better suited for the matrix. In algae oil, direct quantification of peroxides and calculation of PV by ^1H -NMR (Fig. 2) is especially useful to early-mid to later stage oxidation, when secondary oxidation products are formed. In earliest stages of algae oil oxidation, the sensitivity of ^1H -NMR is not ideal: The algae oil is rich in long chained polyunsaturated fatty acids, leading to formation of a wide range of peroxides when oxidized. This is evident in the form of many small peroxide signals in the ^1H -NMR spectrum. A more sensitive method based on ^{19}F -NMR is presented (Fig. 3), aiming for future quality control.

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PV by titration

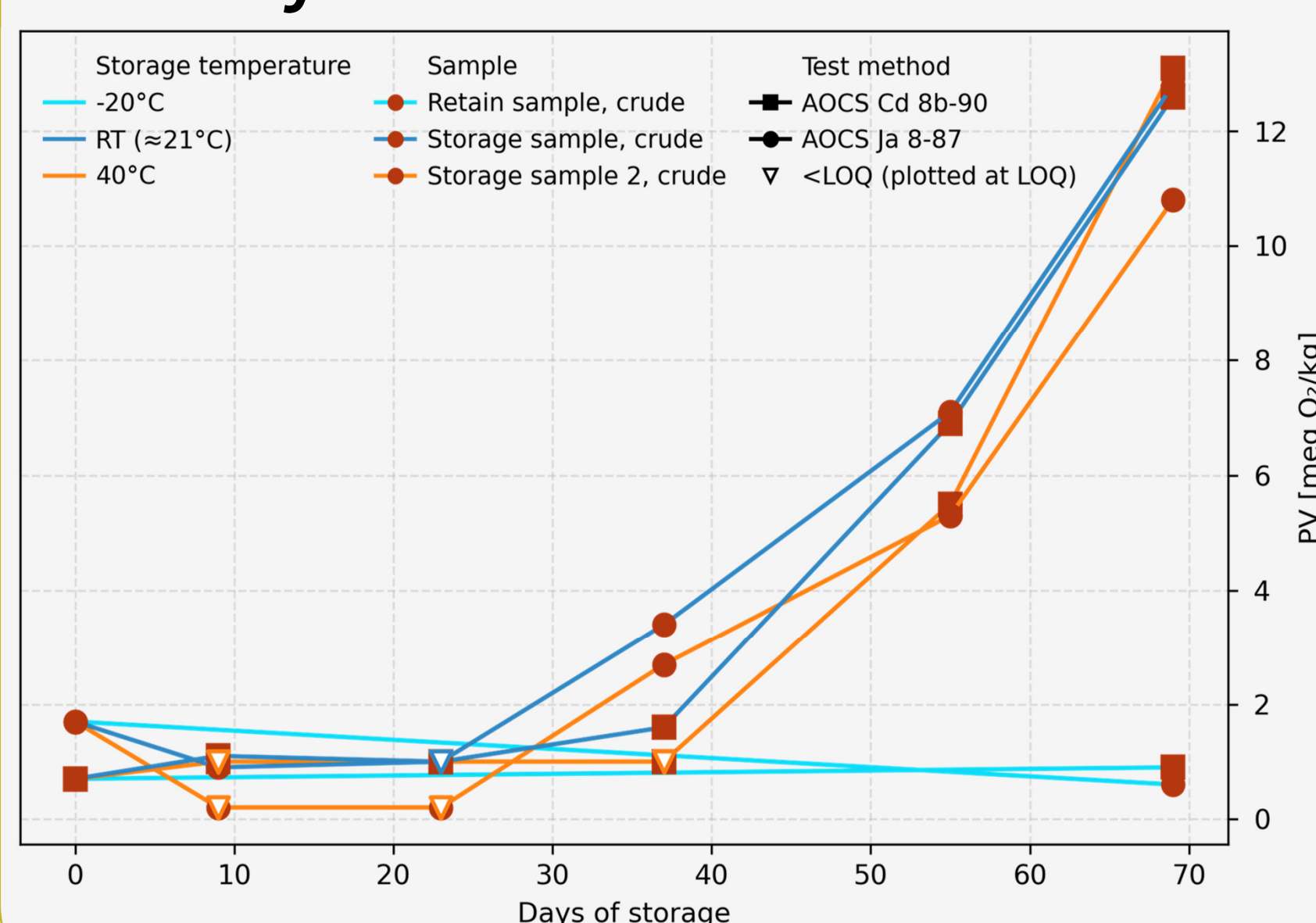


Fig. 1: PV of stored crude algae oil by different titration methods.

Storage & oxidation experiment on crude algae oil

Aim: early detection of peroxides

- Titration: early PV testing
→ no clear results due to specificity and sensitivity
- ^1H -NMR: Specific, just sensitive enough for early PV testing



PV by ^1H NMR

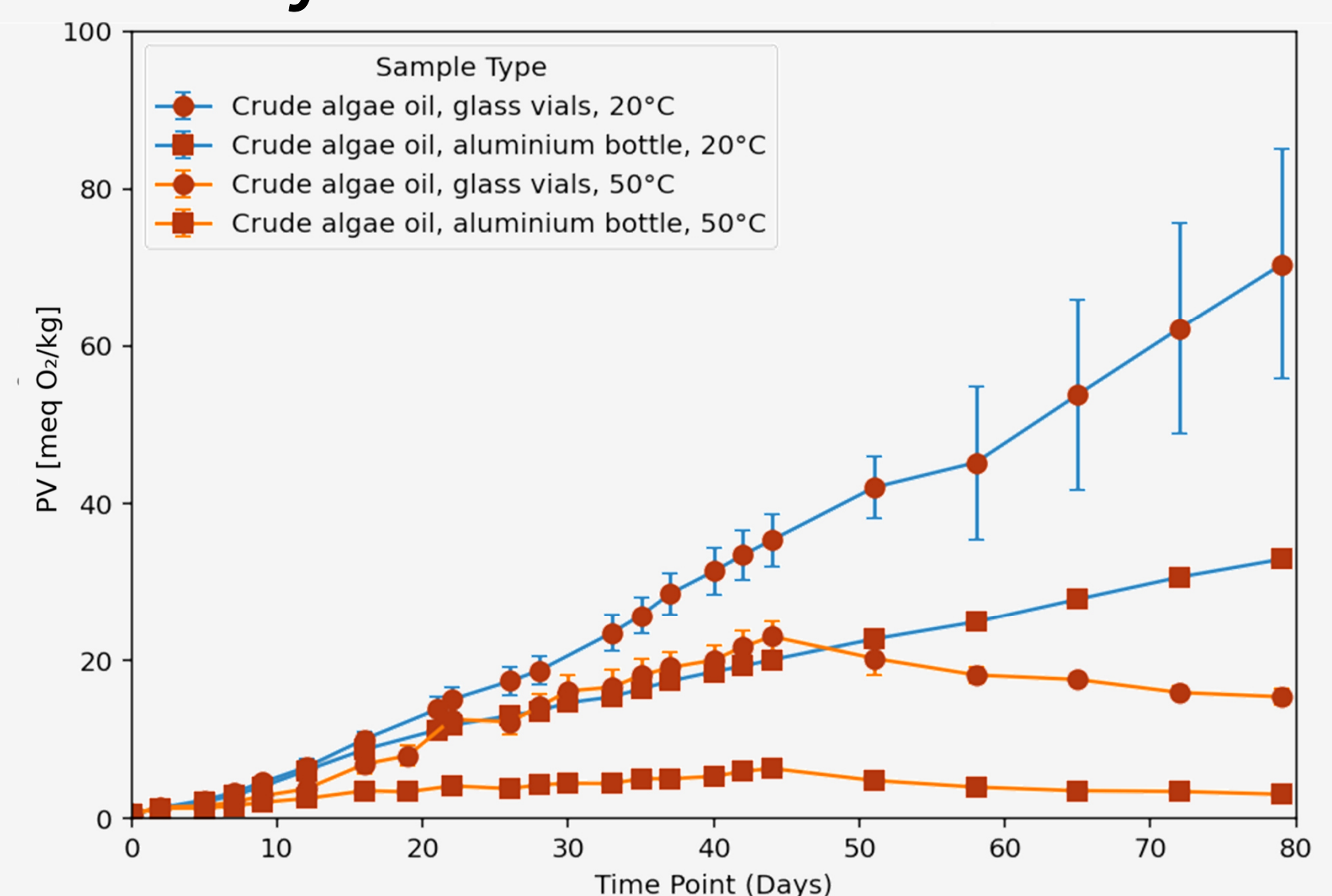


Fig. 2: PV of stored crude algae oil by ^1H NMR (direct measurement).

^{19}F -NMR titration with TTFMPP

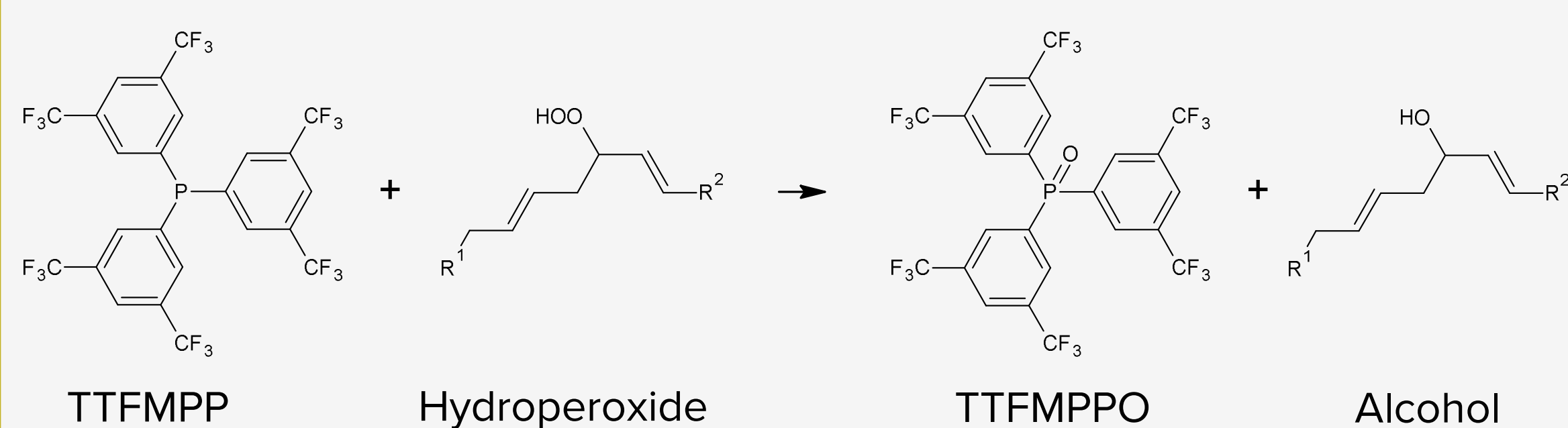


Fig. 3: Reaction of TTFMPP and Hydroperoxide to TTFMPPO and Alcohol

Redox reaction:

4,5-Bis-Trifluoromethylphenylphosphine (**TTFMPP**)

with **hydroperoxides** forms

4,5-Bis-Trifluoromethylphenylphosphine oxide (**TTFMPPO**) and **alcohol** (Fig. 3)

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

Different methods vs ^1H NMR

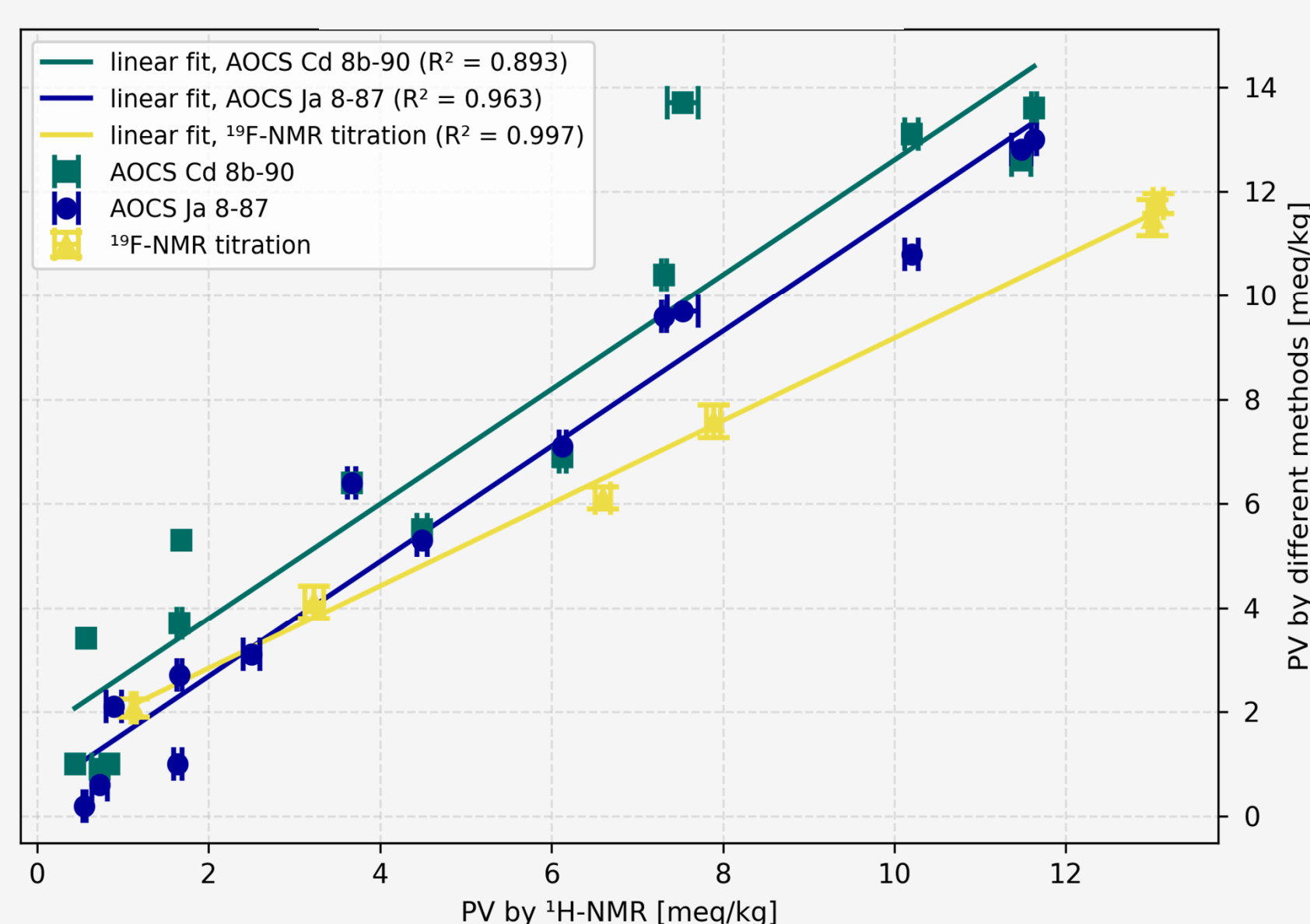


Fig. 5: PV by different methods vs PV by ^1H NMR

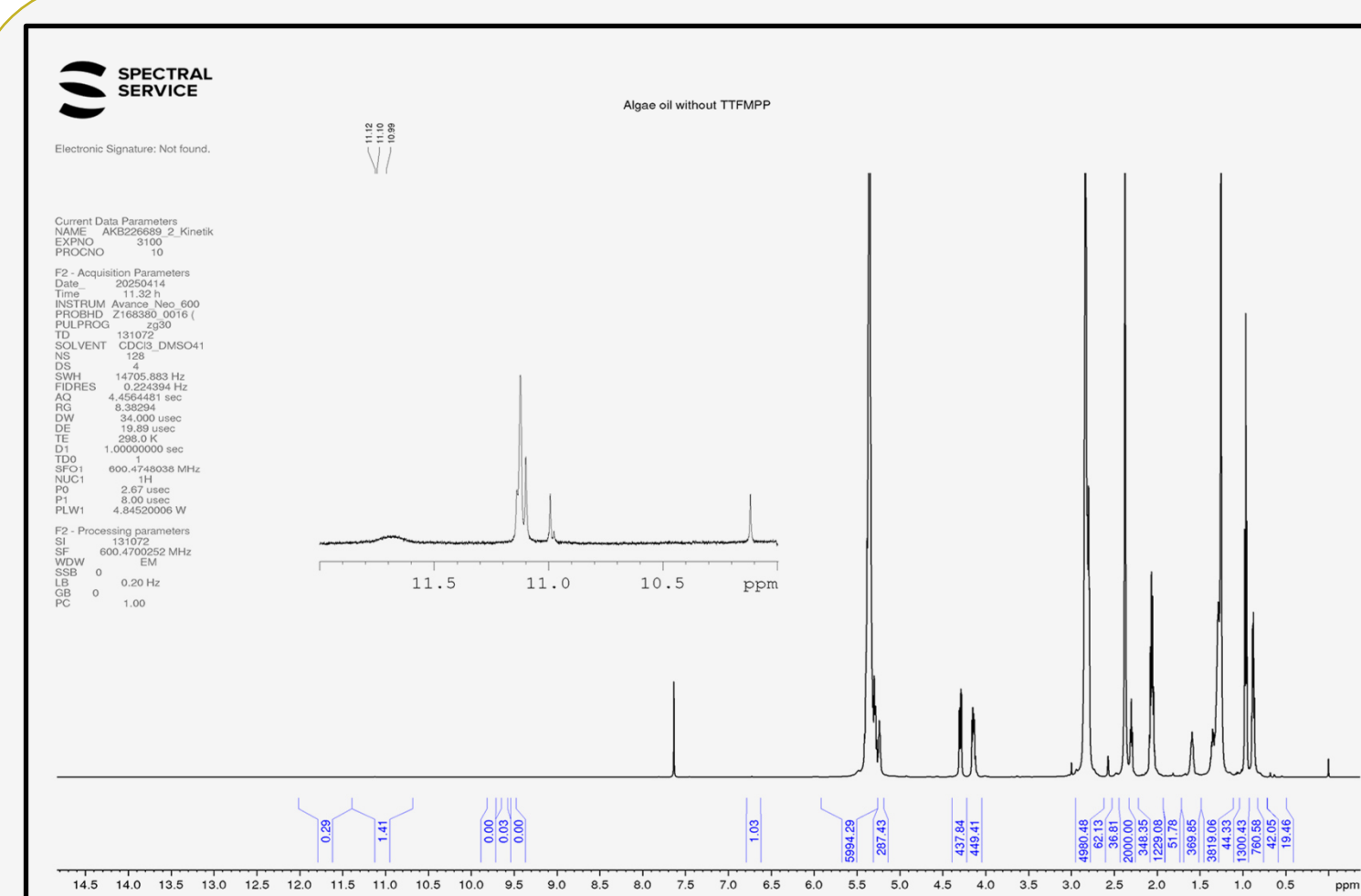


Fig. 4: ^1H NMR spectrum of algae oil, zoom on peroxide region

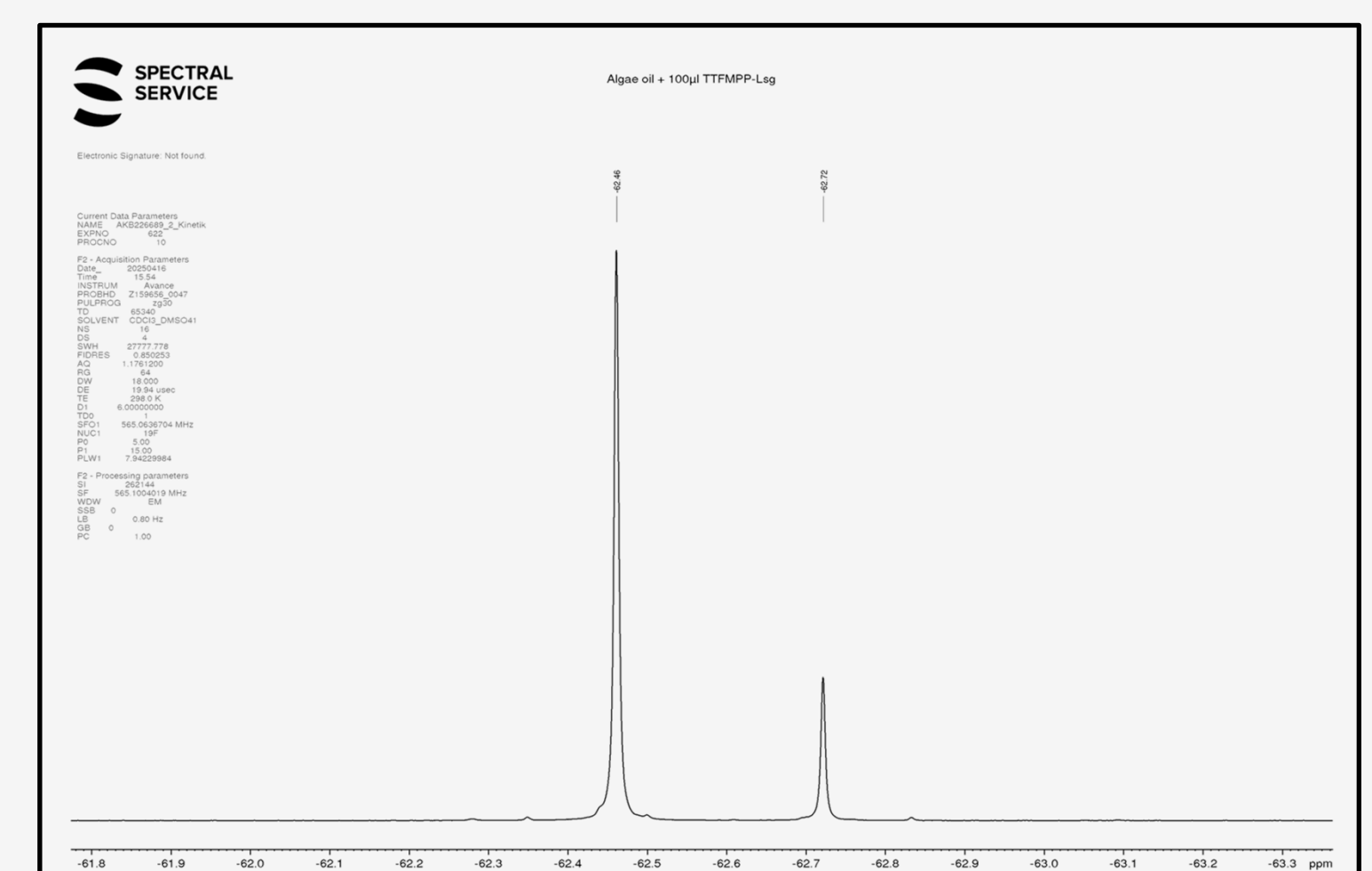


Fig. 5: ^{19}F NMR spectrum of TTFMPP + TTFMPPO in algae oil

- More linear response of ^{19}F NMR titration than classic titration methods
- Influence of other redoxactive compounds on classic titration?
- ^{19}F -NMR titration: Sensitivity increase by more than factor 18 and more accurate results at lower concentrations compared to ^1H NMR

Take-Home Message

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 sensitive than AOCs Cd 8b-90 and AOCs Ja 8-87. In conclusion, the ^{19}F -NMR method for determining the PV has proven to be a viable method for quality control on algae oil.