Rapid quantification of hydroperoxides without standards

A. Chaintreau & M. Calandra

IDEA/ hydroperoxide task force

Brussels, December 3rd, 2015
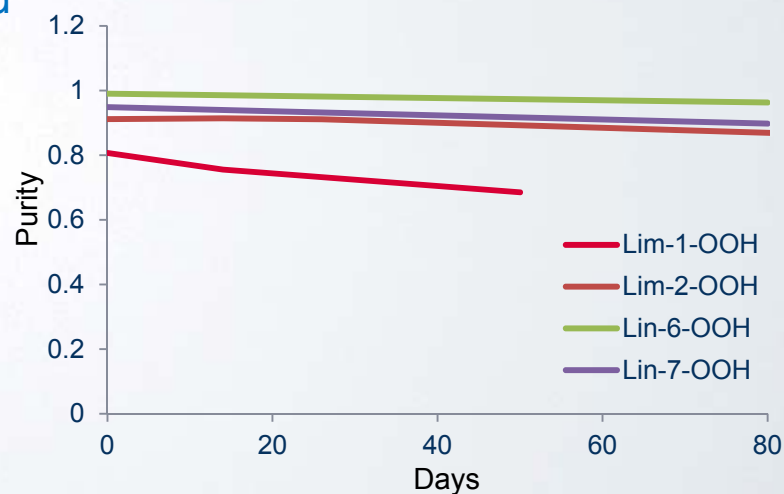
Stability of standards

› Re-Investigation starting from pure standards

› Quantification
  › ^{1}H NMR with an internal standard

› Storage at -80°C
  › Stable for 80 days
  › Except Lim-1-OOH

› Storage at -18°C
  › Less stable
  › Already reported in June

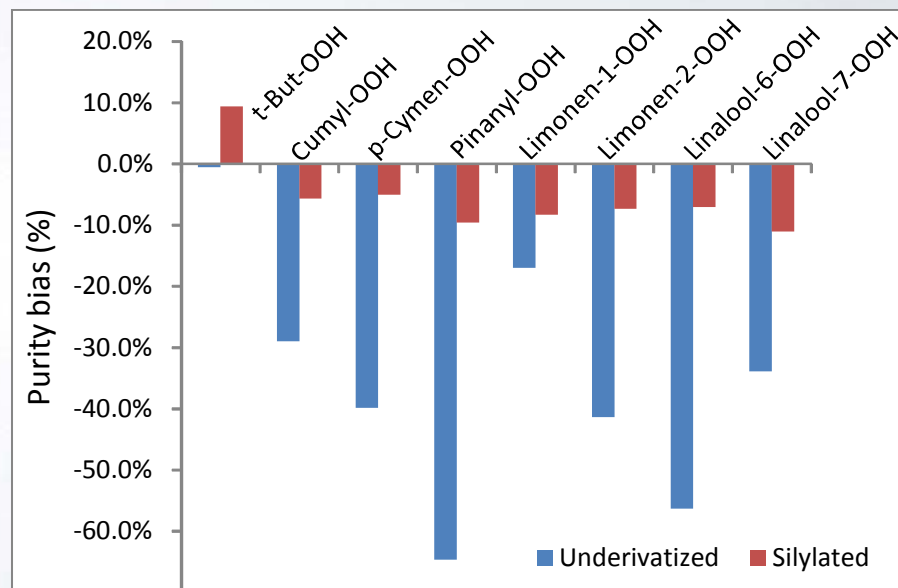Firmenich

Purity by silylation/GC-FID/predicted RRFs

› ^{1}H-NMR + ISTD as reference method

› Without derivatization
  › Biases up to 65%

› After derivatization
  › Biases < ±11%

No standard required !
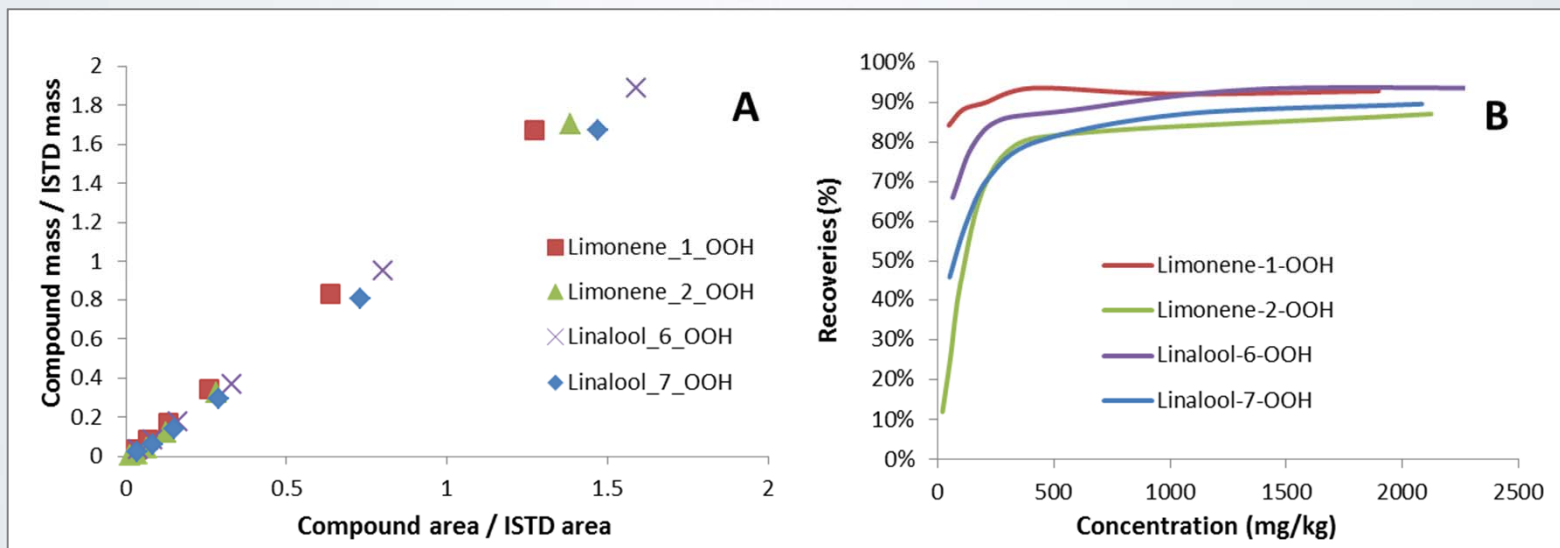
Purity bias (%) chart with categories: t-But-OOH, Cumyl-OOH, p-Cymen-OOH, Pinanyl-OOH, Limonen-1-OOH, Limonen-2-OOH, Linalool-6-OOH, Linalool-7-OOH. Legend: Underivatized (blue), Silylated (red). Y-axis from 20.0% to -60.0%.

Firmenich

Recoveries of calibration solutions

› Good calibration linearities
  › $R^2 > 998$


› Recoveries = Fraction on injected standard reaching the detector
  › Satisfactory recoveries down to 500 ppm
    › Bias < 20%

Quantification in an orange oil

› Low recoveries (reminder)

   › Formation of a peroxyhemiacetal ?

› New (simplified) test
   › Same orange oil + 3000 ppm Lin-2-OOH

   › Adduct quantification by ^{1}H-NMR

> › Disappeance of Lin-2-OOH
> › Formation of an ≈ equivalent molar amount of adduct
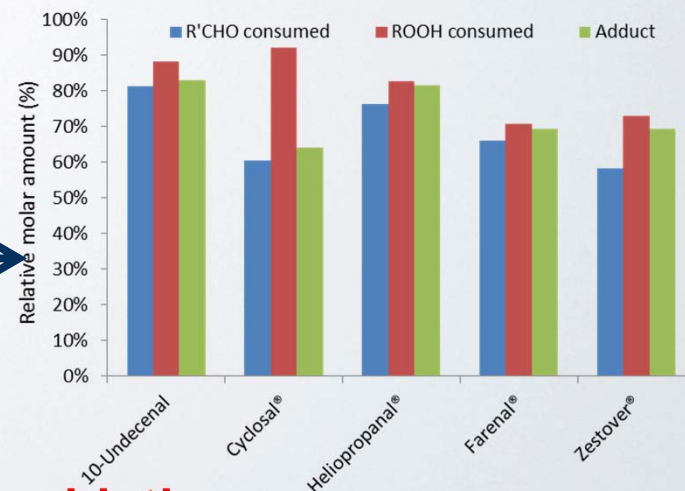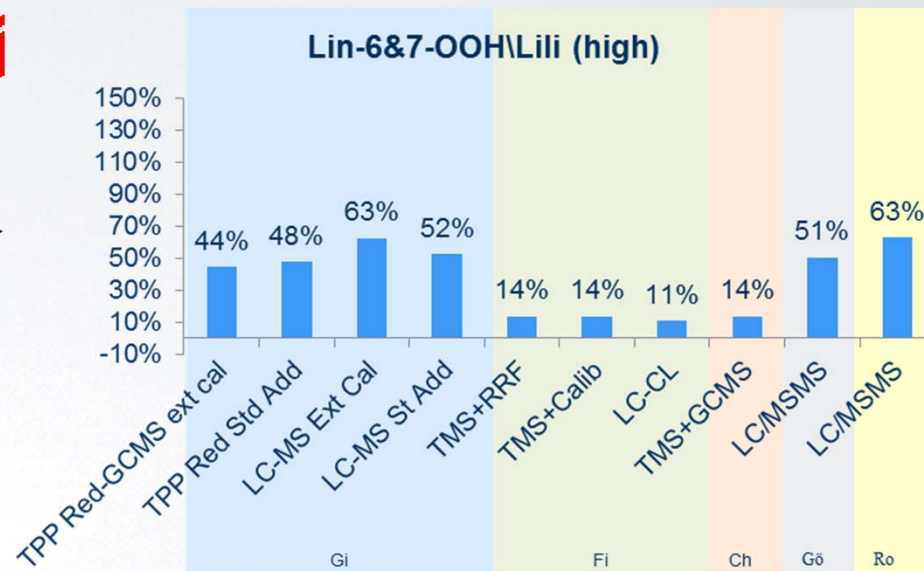
Firmenich
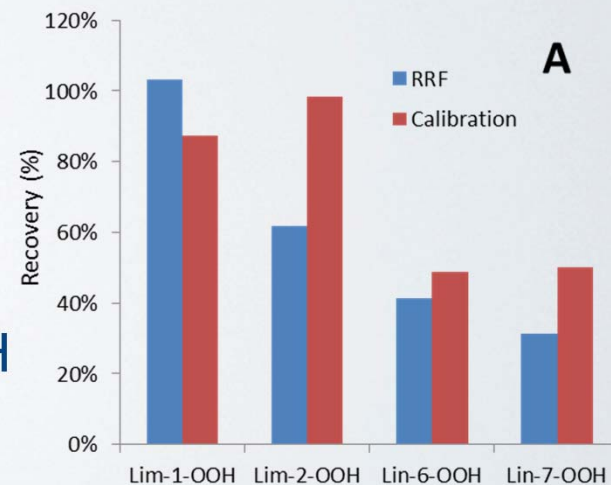
Quantification in Lili

› June meeting ————————➤
   › All recoveries < 100%

› 5 Aldehydes in Lili

› Simplified medium
   › (1 Aldehyde + Lim-2-OOH)/CyHexane
   › ≈ equimolar proportions

> 60-82 % of aldehydes disappear
> ≈ same molar amount of adduct appears

➔ **If ROOHs generated upon terpene oxidation**
                    ➔**Consumed by reaction with aldehydes**

Lin-6&7-OOH\Lili (high)

Bar chart values: 44%, 48%, 63%, 52%, 14%, 14%, 11%, 14%, 51%, 63%
Categories: TPP Red-GCMS ext cal, TPP Red Std Add, LC-MS Ext Cal, LC-MS St Add, TMS+RRF, TMS+Calib, LC-CL, TMS+GCMS, LC/MSMS, LC/MSMS
Groups: Gi, Fi, Ch, Gö, Ro

Second chart legend: R'CHO consumed, ROOH consumed, Adduct
Categories: 10-Undecenal, Cyclosal®, Heliopropanal®, Farenal®, Zestover®

Firmenich

Global conclusions

› ROOH Standards
  › Available in pure state
  › Exact purity by quantitative ^{1}H-NMR with internal standard
  › Rapid purity evaluation by silylation/GC-FID/Predicted RRFs
  › Storage at -80°C

› Rapid quantification of ROOH by silylation/GC-FID/Predicted RRFs
  › Down to 500 mg/kg
  › Underestimation of $\approx$ 20%,   BUT…
  › No need of standard
  › Not applicable to products in protic media

› Chemistry of ROOHs
  › Aldehydes prevent ROOH accumulation in EOs & fragr. oils

→ «**Protection by formulation**» ? (Andreas)

Firmenich

Firmenich
inspiring!

INNOVATIVE CRAFTSMANSHIP IN FRAGRANCES AND FLAVORS SINCE 1895