

APPENDIX 1 to the IFRA Method for the determination of the peroxide value (POV)

Outline of factors that may influence POV results in typical laboratory test procedures

Following a publication by M. Calandra et al. on a HPLC method for hydroperoxides derived from limonene and linalool in citrus oils¹, highlighting some potential limitations in the IFRA method related to POV determination, it is therefore relevant to provide additional information as to the impact of certain parameters used in the POV titration method.

As previously explained the POV determination is dependent on various parameters. Setting these parameters enables homogenous results to be obtained throughout different analytical labs (whether QC or external ones). Obviously, this method has some limits that will impact the absolute determination of the POV value but allows any QC type lab to perform such analysis for the purpose of quality control.

The following outlines the parameters that may influence the POV result determined in laboratories operating with modified methodologies compared to the IFRA method due to the adoption of different operating parameters.

Sample size

Peroxide value depends on sample size; it decreases with increased sample size due to several phenomena²:

- I₂ fixation on double bonds
- Further oxidation of the fat by dissolving oxygen
- O₂ absorption on the sample (large surface area to volume ratio)
- Sample Solubility

To take into account this fact, the sample size in the IFRA revised method was fixed to 3 g with the objective of:

- Avoiding POV variability that might be observed in other methods where sample size fits the target POV³
- Obtaining the highest values compared to other methods with fixed higher sample amounts⁴ (5-10g)

Reaction time

Peroxide value depends on reaction time. Decreasing this time will lead to lower and less accurate POV. This is due to⁵:

- Difference of reactivity of peroxides with iodide ions:

Peracids > hydroperoxides > ozonides > peroxyesters > diacylperoxides > α-hydroxyalkylperoxides > dialkylperoxides > cyclic peroxides

- Oxygen effect in absence of air protection

As mentioned in 2003 by Fiebig⁶, it is well known that a one-minute reaction time is not sufficient to allow complete reaction, *“Fortunately, the reaction time has been standardized within international methods to 1 minute, even if lower PV is obtained.”* Indeed, this reaction time is proposed in the main

official methods on POV determination.⁷ Most of specifications on POV, including IFRA standards, have been developed with this one-minute reaction time explaining the rationale for keeping this reaction time in the revised IFRA method.

Oxygen effect

Peroxide value can increase by the so called “oxygen effect”⁸. Indeed, the presence of oxygen in the reaction media can lead to iodine release from KI by O₂ present in the solution as described in Equation 1.

Even if this effect seems more important in presence of peroxydes⁹, the “blank subtraction” described in most of the methods, including the IFRA one, is a way of decreasing its impact while not completely removing it.

Equation 1 : Competitive reaction observed during POV determination in presence of oxygen



Other parameters

Other parameters may also impact the POV determination. Therefore, it is really important to ensure the parameters in the described method are maintained to avoid negatively impacting the accuracy. Among those parameters, one could list the following ones¹⁰:

- Iodide⁻ origin: KI seems better than NaI for titration due to its better solubility in the organic solvents used in the method
- Light: the kinetic of the reaction is increased in presence of light
- Temperature: the kinetic of the reaction is increased with temperature, therefore a thermostated room or specific location might be preferred for POV determination
- Indicator: Potato starch for iodometry produces a deep blue color in the presence of the iodonium ion and is thus recommended for the titration compared to other starches
- Residual water: presence of water in the sample, in the flasks etc. can decrease the kinetic of the reaction leading to lower POV
- Solvent can affect POV due to¹¹:
 - ✓ Lack of sample solubility → lower POV
 - ✓ Time required for titration longer with isooctane → lower POV
 - ✓ Solvent and acid grades
 - ✓ Mixture stability
- Titration solution: method precision can be related to titer solution

These are all factors which may influence the POV result for any given material. It is therefore important that laboratories applying such methodology are both aware of the potential that these have on the final value obtained, together with the reasons for variability seen between laboratories individual results for the same sample.

References:

1. Calandra et al, **Flavour Fragrance J.**; **2016, 31:241 -249**
2. L. Lowen et al. **Ind. Eng. Chem.**; **1937, 29:151**; Dastur and Lea, **Analyst** **1941; 66:90**; Stansby **Ind. Eng. Chem. Anal. Ed.** **1941, 13:627**; R. W. Riemenschneider et al. **Oil & Soap**; **1943, 169-170**; R. F. Paschke, D. H. Wheeler, **Oil & Soap** **1944, 21: 52.**; C. H. Lea, **J. Chem. Technol. Biotechnol.**; **1946, 65:286**; F. E. Volz, W. A. Gortner, **J Am Oil Chem Soc** **1947, 24, 417.**; C.D. Wagner et al. **Anal. Chem.**; **1947, 19:976**; A. Seher, **Fette, Seifen, Anstrichm.**; **1958, 60 :264.**; F.H.L. Van Os, C. Scholtens, **La France et ses Parfums**; **1959, 30:34**; R. D. Mair, A. J. Graupner, **Anal. Chem.**; **1964, 36:194.**; T. D. Crowe, P. J. White, **J Amer Oil Chem Soc**; **2001, 78:1267.**; **ISO 3960:2007 and 2017**
3. **ISO 3960:2007 and 2017**; **ISO 18321:2015**, European Pharmacopeae- Method B; AOCS Cd 8b-90
4. European Pharmacopeae- Method A; AOCS Cd 8-53; Food Chemical Codex (2003)
5. R. W. Riemenschneider et al. **Oil & Soap**; **1943, 169-170**; R. F. Paschke, D. H. Wheeler, **Oil & Soap**; **1944, 21:52**; C. H. Lea, **J. Chem. Technol. Biotechnol.**; **1946, 65:286**; F. E. Volz, W. A. Gortner, **J Am Oil Chem Soc**; **1947, 24:417.**, C.H. Lea, **J.Sci. Fod Agric.**; **1952, 586-593**; R. D. Mair, A. J. Graupner **Anal. Chem.**; **1964, 36:194**; R. M. Johnson, in **The Determination of Organic Peroxides** **1970, 7-14 and 15-28.**
6. Chairman of the ISO/TC34/SC11: Animal and Vegetable Fats and Oils in charge of the ISO norm 3960 on POV of fats
7. **ISO 18321**; **ISO 3960**; European Pharmacopeae ; AOCS Cd 8-53 ; AOCS Cd-98B
8. Stansby **Ind. Eng. Chem. Anal. Ed. ; 1941, 13, 627**; R. W. Riemenschneider et al. **Oil & Soap**; **1943, 169-170**; C. H. Lea, **J. Chem. Technol. Biotechnol.**; **1946, 65: 286**; J.H. Skellon, **Analyst**; **1948, 73:78-86**; R. M. Johnson, in **The Determination of Organic Peroxides**; **1970, 7-14 and 15-28**, T. D. Crowe, P. J. White, **J Amer Oil Chem Soc**; **2001, 78:1267.**
9. T. D. Crowe, P. J. White, **J Amer Oil Chem Soc** **2001, 78:1267.**
10. Stansby **Ind. Eng. Chem. Anal. Ed.** **1941, 13, 627**; R. F. Paschke, D. H. Wheeler, **Oil Soap** **1944, 21, 52**; C. H. Lea, **J. Chem. Technol. Biotechnol.** **1946, 65, 286**; C.D. Wagner et al. **Anal. Chem.** **19, 976, 1947**; J.H. Skellon, **Analyst**, **1948,73, 78-86**; Mair, **1964**; R. M. Johnson, in **The Determination of Organic Peroxides**; **1970, 7-14 and 15-28**; AACC method 58-16.
11. Stansby **Ind. Eng. Chem. Anal. Ed.**; **1941, 13:627**; A. Seher, **Fette, Seifen, Anstrichm.**; **1958, 60:264.**