Automated Anaerobic Iodometric Determination of Lipid Hydroperoxides

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The formation of hydroperoxides in lipids as well as their relevance for sensory and nutritional deterioration has been recognized more than a century ago. Owing to their importance, numerous approaches for their analytical determination have been devised, the oldest one being iodometry, all of them troubled with problems of their own - be it selectivity, sensitivity or economic efficiency.

Our aim was to apply automation, titration under inert atmosphere and catalysis to the iodometric approach (peroxide value, PV in meqO_2/kg) to lower the necessary amount of fat and to increase productivity without impairment of accuracy.
One of the most troubling features of the conventional iodometric method is the known dependence of the PV on the sample weight of fat. Therefore, standardized methods demand using portions of about 5g (or even 10g for PV<1) to be analyzed, thus entailing enormous efforts in fat extraction, especially for low-fat products. Starting point of our experiments was to investigate the relationship thiosulfate consumption vs. sample weight, which was found to be strictly linear. The non-linearity of the relationship PV vs. sample weight, has thus to be attributed to the erroneous blank value entering the calculation.
Furthermore, variation of the time allocated for the reaction between iodide and lipid hydroperoxides showed that the mandatory 1 min is by far not sufficient for complete conversion of peroxides. This can be compensated via automated titration allowing stricter control of reaction time, thus reproducibility is enhanced. Catalysis by traces of molybdate was found to speed up the reaction between iodide and lipid hydroperoxides [1] considerably but renders method even more different from conventional method.
In addition, the well known oxygen error, which becomes increasingly important for smaller amounts of hydroperoxides, was prevented by purging both reagents and titration vessel using argon. Inert gas purging has been applied before [2], yet argon is advantageous as it allows open beakers to be used due to its higher density. Flow of argon was conveniently controlled from tiamo 2.5 software using magnet valves.
Existing problems due to compounds like thymoquinone or hydroxytyrosol, present in *Nigella sativa* and *Olea europaea*, respectively, are still not resolved by this more sophisticated iodometric method. Thus additional methods based on, e.g. NMR, are being developed by us. First results of these approaches are also presented.

References:

[1] A.O. Allen, C. J. Hochanadel, J. A. Ghormley, T. W. J. Davis, *Phys. Chem.* **1952**, 56, 575-586
[2] S. Hara, Y. Kuroda, S. Nakagawa, Y. Totanij, *J. Jpn. Oil Chem. Soc.* **1994**, 43(1), 18, F. W. Heaton, N. Uri *J. Sci. Food Agric.* **1958**, 9, 781