Chemiluminescence method to detect lipid oxidation in milk and cream powder

Helena Stoffers, Patrizia Piccinali, Yves-Alain Brügger, Katharina Breme, Dominik Guggisberg
Agroscope Liebefeld-Posieux Research Station ALP-Haras, Berne, Switzerland
helena.stoffers@alp.admin.ch

Introduction

Lipid and protein oxidation are limiting factors for the shelf-life of milk and cream powder. Oxidative changes are often not detected until formation of odor-active secondary oxidation products. A new approach to detect non-odor-active primary oxidation products (hydroperoxides) is chemiluminescence (CL). During decay of peroxide radicals, excited electrons relax into their thermodynamically preferred state by emitting photons, which are counted by a photomultiplier tube.

Objectives

The goals of this study were to

- test the suitability of CL to detect oxidation in milk and cream powder
- compare CL and sensory evaluation
- confirm oxidation by detecting volatile compounds known to be secondary oxidation products by headspace solid-phase microextraction-gas-chromatography-mass spectrometry (HS-SPME-GC-MS)

Material and Methods

Roller-dried whole milk powder was illuminated (fluorescent lamp Philips TL 40W/33RS, 2000 LUX, 18cm distance to the samples) at 30°C during 2, 14, 16, 18, 20 and 21 h to induce photo-oxidation. A trained panel (*n*= 13–18) tested the samples directly after the treatment performing triangle tests with treated versus untreated samples. For CL analysis, 100mg of pelletized milk powder (pressure 800 kg/cm^2) were placed in the chemiluminescence instrument (ACL Instruments, Kerzers, Switzerland) directly after illumination. The sample was heated from room temperature to 180°C (heating rate 0.5°C / min, N_2 gas flow) and the amount of emitted photons was counted in a photomultiplier tube. In an additional test, spray-dried cream powder was illuminated as described above for 0, 1, 2, 3, 5 and 11 days and analyzed with CL. Volatile compound profiles were measured by HS-SPME-GC-MS using a divinylbenzene/carboxene/polydimethylsiloxane 50/30µm 2cm fiber to confirm oxidative changes.

Results and Discussion

After 2 h of illumination of roller-dried whole milk powder, CL measurements (Fig. 1) already showed altered signals compared to the reference, whereas the trained sensory panel detected a significant difference after 18 h of treatment only (Tab. 1). The result is not surprising as the panelists perceive odor-active secondary oxidation products, while CL measurement is focused on the decay of primary oxidation products (hydroperoxides). Pelletizing of powder improved reproducibility of CL measurements as a defined powder surface was exposed to the light. As signal intensity was low, results have to be verified and compared to additional methods.

Tab 1: Results of sensory triangle test performed by a trained panel (*n*= 13–18)

Illum. time [h]	2	14	16	18	20	21
No. of testers (*n*)	15 / 14	15 / 14	13 / 18	13 / 18	13 / 18	15 / 14
Correct answers	5 / 8	7 / 6	7 / 15*	8* / 14*	8* / 10*	12* / 10*
*** significant difference compared to reference (alpha = 0.05)**						

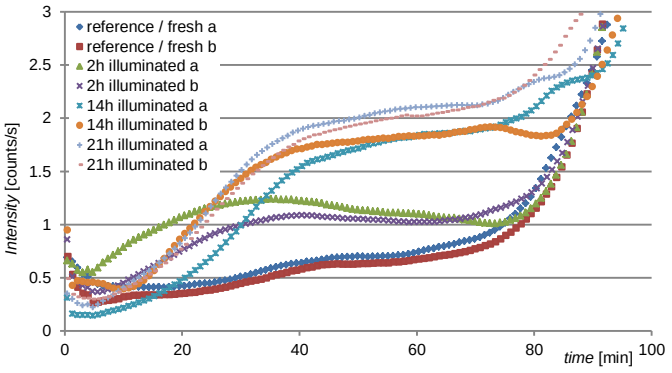

Fig. 1: CL-Measurements of roller-dried whole milk powder (heating rate 0.5°C/min, N_2 gas flow)

Another test with spray-dried cream powder showed clear differences in CL signal after 1 d of illumination (Fig. 2). Intensity of CL signal increased and oxidation induction time decreased with longer illumination time. HS-SPME-GC-MS results confirmed oxidative changes of lipids by detecting clearly higher signals of saturated and unsaturated aldehydes C3–C9 which are known to be secondary oxidation products (Fig. 3).

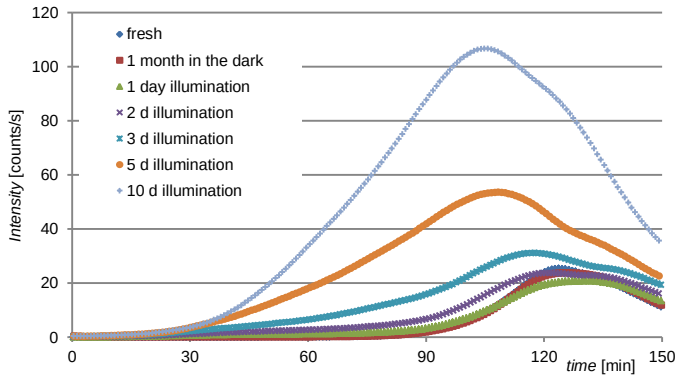

Fig. 2: CL-intensity of spray-dried cream powder show clear differences depending on illumination time (heating rate 0.5°C/min, N_2 gas flow)

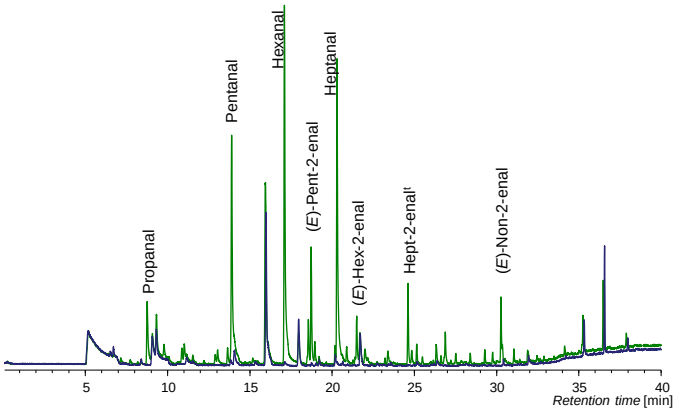

Fig. 3: Overlay of HS-SPME-GC-MS-chromatograms (total ion current TIC) of cream powder samples.
blue chromatogram: non-oxidized powder kept under argon in the dark at 4°C
green chromatogram: oxidized powder (5d of illumination under oxygen at 30°C)
t= tentatively identified without reference compound injection.

Conclusions

The new approach with chemiluminescence (CL) method allowed to detect lipid oxidation at an earlier stage than sensory evaluation as CL focuses on primary oxidation products (hydroperoxides) whereas the sensory panelists perceive odor-active secondary oxidation products. CL might hence be a tool for monitoring powder quality, since sample preparation is very simple and results are reproducible. Results still have to be confirmed and compared to additional methods. Further investigation regarding stability prediction, using synthetic air for gas flow, are planned.

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