The influence of autoxidation on milk fat composition

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1. Introduction

The autoxidation of fat is a process affecting quality in an unfavourable way. The reaction with oxygen leads to formation of hydroperoxides and a variety of secondary oxidation products with negative effects on flavour and nutrient properties (1-5).

In this paper the dependence of autoxidation processes in milk fat upon exposure to daylight (6,7) and the resulting time resolved changes in peroxide value, ultraviolet absorbance, triglyceride contents and fatty acid composition will be described. The constancy of fatty acid composition is important for the characterization of fat samples. Furthermore the effect of rising peroxide values on triglyceride contents is of great interest with regard to detection of foreign fats in milk fat by quantitative triglyceride analysis (8,9). Another aspect is the preparation of a fat reference material, e.g. for that method, which has to remain unchanged over a long period.

Since the oxidative stability of fat depends on the iodine value (1), it is interesting to analyze samples obtained from butter of different feeding periods. Milk fat from the winter period has a smaller amount of triglycerides with a total acyl carbon number of 54 than a summer fat, which is equivalent to a lower content of unsaturated fatty acids.

Finally the relation between peroxide value and ultraviolet absorbance with progressing air exposure will be shown for two different milk fats (10,11).

2. Materials and methods

2.1 Milk fat samples

All milk fat samples were obtained by melting butter and filtering the fat layer at 50°C in the dark.

2.2 Determination of ultraviolet absorbance (12)

Solutions were prepared by dissolving an amount of milk fat in 2,2,4-trimethylpentane (iso-octane), generally 0.01 to 0.20 g per 25 ml, necessary to obtain absorbance values between 0.2 and 0.8. UV absorbance was measured in a cell of 1 cm at 232 nm (hydroperoxides) and 268 nm (secondary oxidation products) against iso-octane. Absorbance values were normalized upon a solution of 1 g fat per 100 ml.

2.3 Determination of peroxide value (13)

After reaction of the fat samples with potassium iodide in a mixture of trichloromethane and acetic acid, the iodine built by the peroxides was titrated with sodium thiosulfate at room temperature. Peroxide values are given in meq O/kg.

2.4 Determination of triglyceride contents

Triglyceride analyses (8) were performed on a Packard 439 gas chromatograph equipped with flame ionization detector, splitless injection port and a 50 cm x 2 mm packed glas column filled with 3 % OV-1 on 100/120 mesh Gas Chrom Q. Nitrogen carrier gas flow was 35 ml/min, detector and injector temperature both 370°C. Temperature program: 210°C, 1 min isothermal, then 6°C/min up to 355°C, followed by 4 min isothermal. Sam-

ples (0.5 ml) of 5 % fat in heptane were injected using the so-called 'hot-injection-technique' (8,9). GC standard: Eight different saturated triglycerides were used (Nu Check Prep. Inc., Elysian MN 56028, USA). With these components a milk fat was standardized as calibration sample. By calibrating three times every day with this milk fat (the third run was chosen) well reproducible quantitative results could be obtained. Triglycerides with odd acyl carbon numbers were added to the respective preceding triglyceride with an even carbon number. The low C56 contents, being less reproducible, were ignored. The remaining triglycerides, including cholesterol, were normalized to 100%. Integration was performed using a Hewlett Packard 3365 II Chemstation.

2.5 Determination of fatty acid composition

Milk fat samples were treated with sodium methoxid (14,15) to get the fatty acid methyl esters (FAME). Analyses of FAME were carried out immediately on a Carlo Erba HRGC 5300 gas chromatograph equipped with split injector, flame ionization detector and a 50 m x 0.25 mm fused silica capillary column coated with CP-Sil 88 (df = 0.20 µm). For carrier gas hydrogen with a flow of 1.6 ml/min and a split ratio of 1:100 was used. Temperature of injector and detector was 255°C. Program: 50°C, 1 min isothermal, then 5°C/min up to 225°C, finally 15 min isothermal. Calibration was performed by use of a test mixture containing the methyl esters of the main fatty acids of milk fat in the naturally occurring ratio. Correction factors were calculated only for these main components, the smaller peaks were not corrected. A Hewlett Packard 3365 II Chemstation was used for integration.

2.6 Reaction times

Night time periods of about 8 hours are included in reaction times of light induced oxidation.

3. Results and discussion

Molten milk fat portions of 15 g were filled in small glasses with a surface of approximately 3.5 cm^2 towards gas phase. The glasses were rinsed with nitrogen, closed and kept in the dark. After solidification all samples of a run, consisting of several glasses of each milk fat, were opened at the same time and exposed to air and indirect sunlight coming through a window pane at room temperature (22°C). Peroxide values and UV absorbances were measured immediately after the end of different reaction times, whereas analyses of triglycerides and fatty acids were made after short-term storage of the reclosed and nitrogen rinsed glasses at -18°C in the dark .

Fig. 1 shows the time resolved peroxide values (PV) for a milk fat from the winter feeding period and a transition period fat. A continuous increase in PV is to be seen for both fats with the rise getting slower however. This may partly be due to saturation of the samples. Another aspect is the enormous decrease in peroxide formation during the night, i. e. in the dark, as will be shown later on.

In Fig. 2 the changes in UV absorbance of hydroperoxides at 232 nm are plotted for the same milk fats. The graphs are showing good parallelism but a quite different look compared with Fig. 1. There are at least two extrema followed by a continuous increase, and although the winter fat produces higher PVs, the values of UV absorbance at 232 nm are evidently lower than those of the transition fat. That means that there is no direct correlation between PV and UV absorbance (Fig. 3). However for long-term measurements there seems to exist a positive rise for both parameters, so simple stability control is also pos-

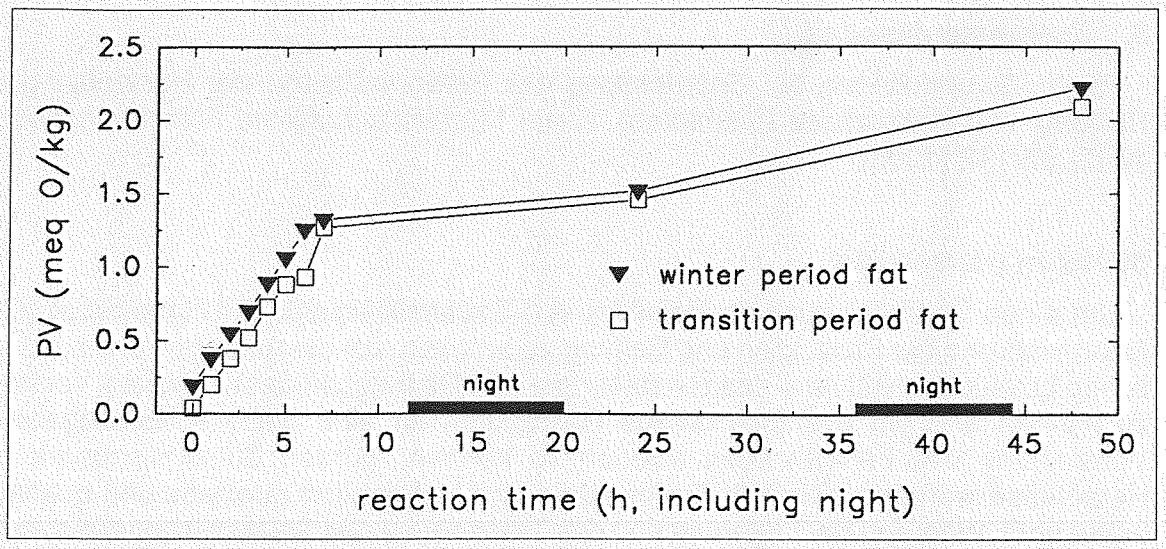

Fig. 1: Changes in PV by light induced autoxidation

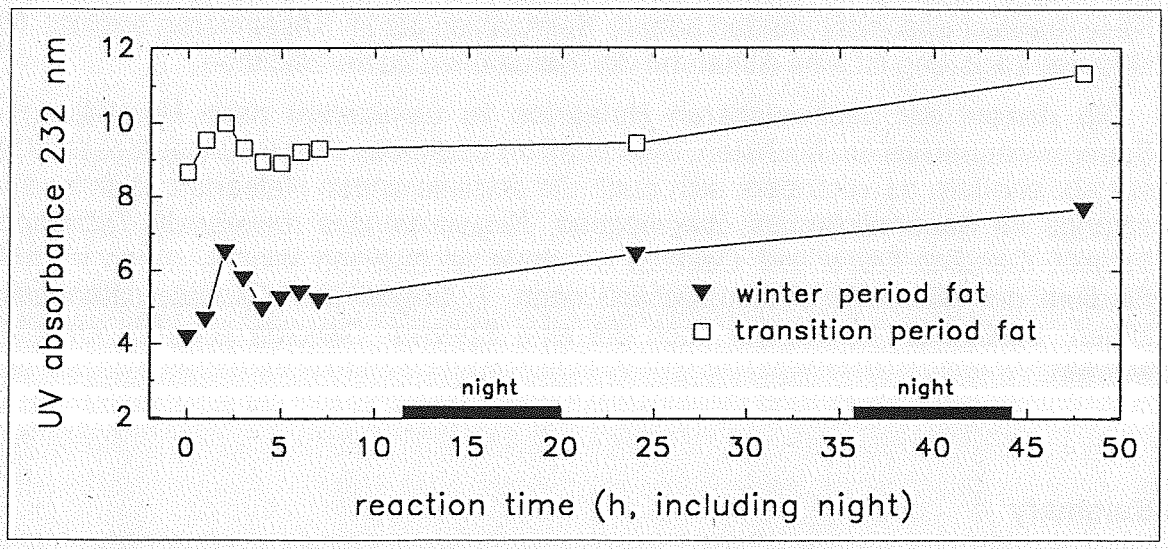

Fig. 2: Changes in UV absorbance at 232 nm by light induced autoxidation

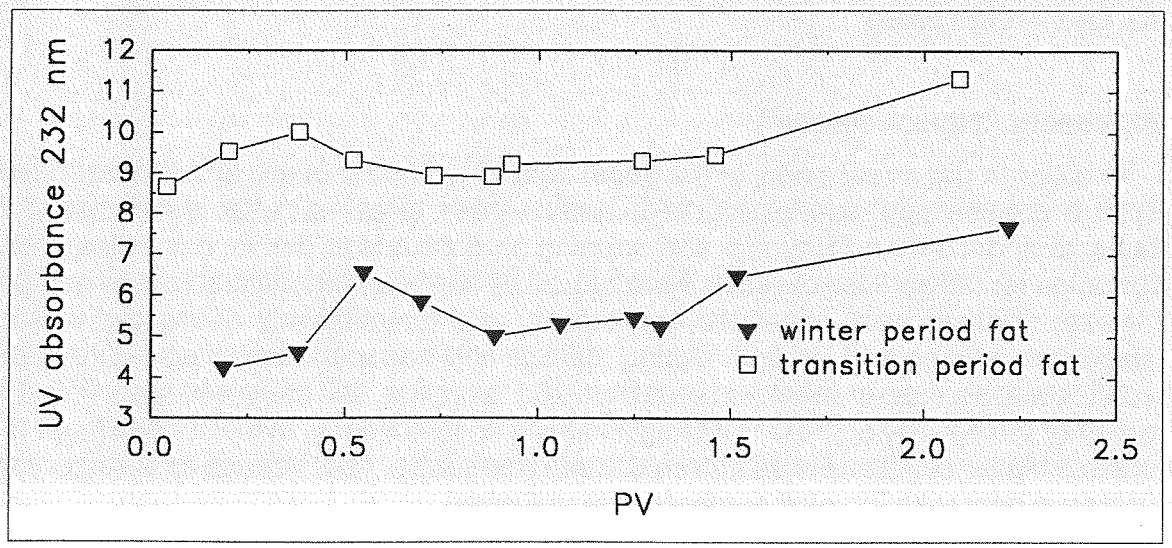

Fig. 3: Correlation of PV and UV absorbance (232 nm)

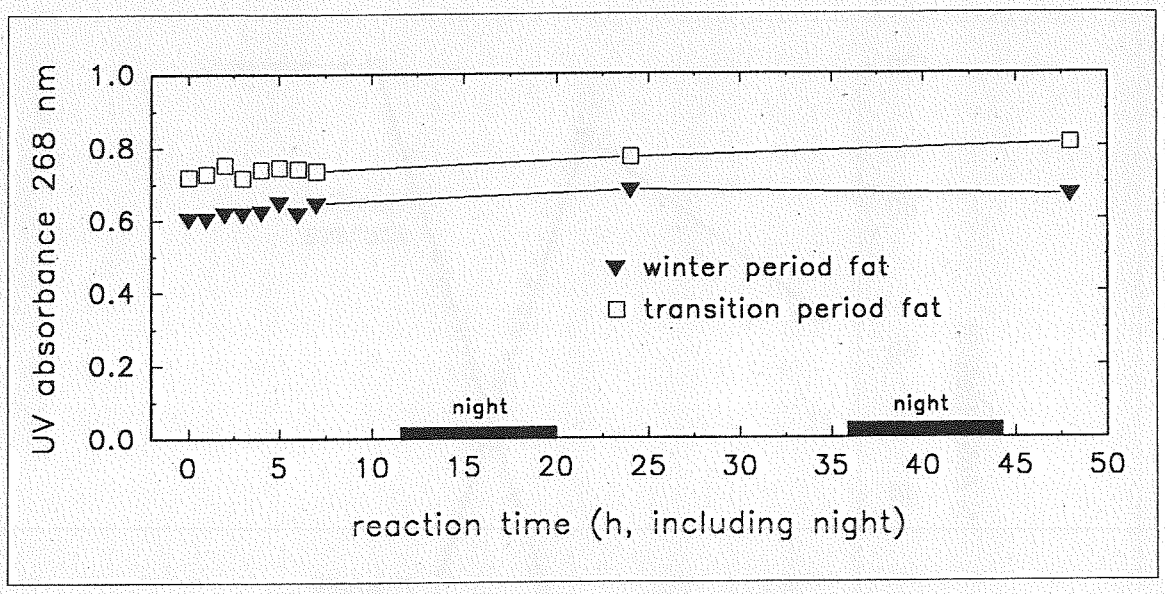

Fig. 4: Changes in UV absorbance at 268 nm by light induced autoxidation

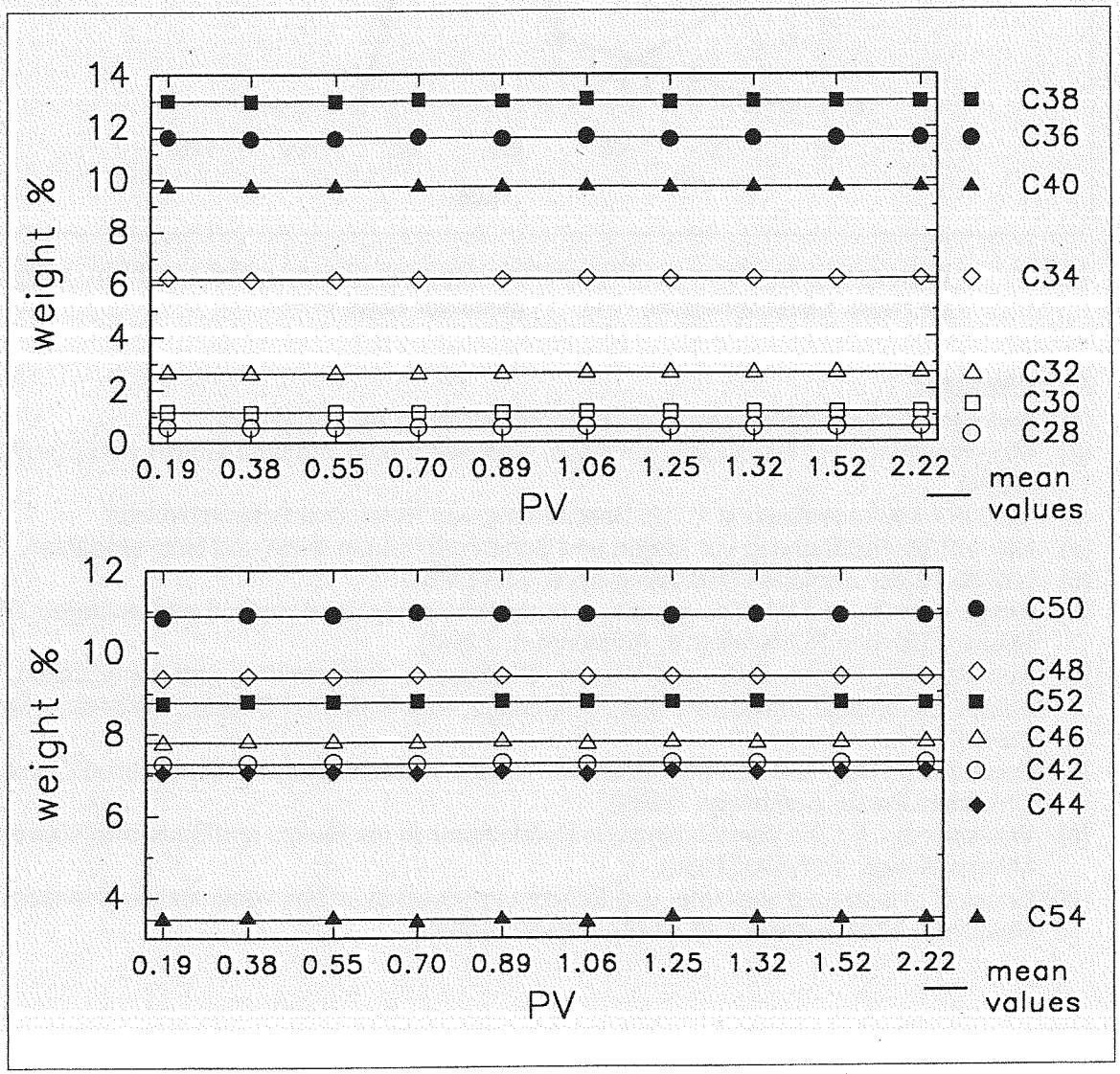

Fig. 5: Triglyceride contents of a winter period milk fat with rising PV

sible by only recording the UV absorbance. As the PV of the winter fat is higher, but the UV absorbance is lower than with the transition fat a correlation of these parameters between different fats is totally impossible.

The reason for the different behavior of these parameters is that UV absorbance only records conjugated hydroperoxides and their absorbance is overlaid by other species with a conjugated diene structure (12).

Fig. 4 shows the UV absorbance at 268 nm, that indicates the amount of secondary oxidation products. The slight rise for both fats results from a rather slow reaction of the arising hydroperoxides.

Quantitative triglyceride analysis in combination with triglyceride formulae is a rather sensitive method for detection of animal or vegetable fat in milk fat (8,9). A prerequisite for disclosing adulterated fats even after long-term storage is the constancy of triglyceride contents. Fig. 5 and 6 show the triglyceride contents of a winter period and a transition period milk fat with rising peroxide value. There is rather no change to be seen within the range of PV. Numeric values are listed in Tab. 1 and 2. Whereas column SD_1 exhibits the standard deviations of triglyceride contents among the differently oxidized milk fat samples, column SD_2 gives the standard deviations for 9 successive analyses of the starting

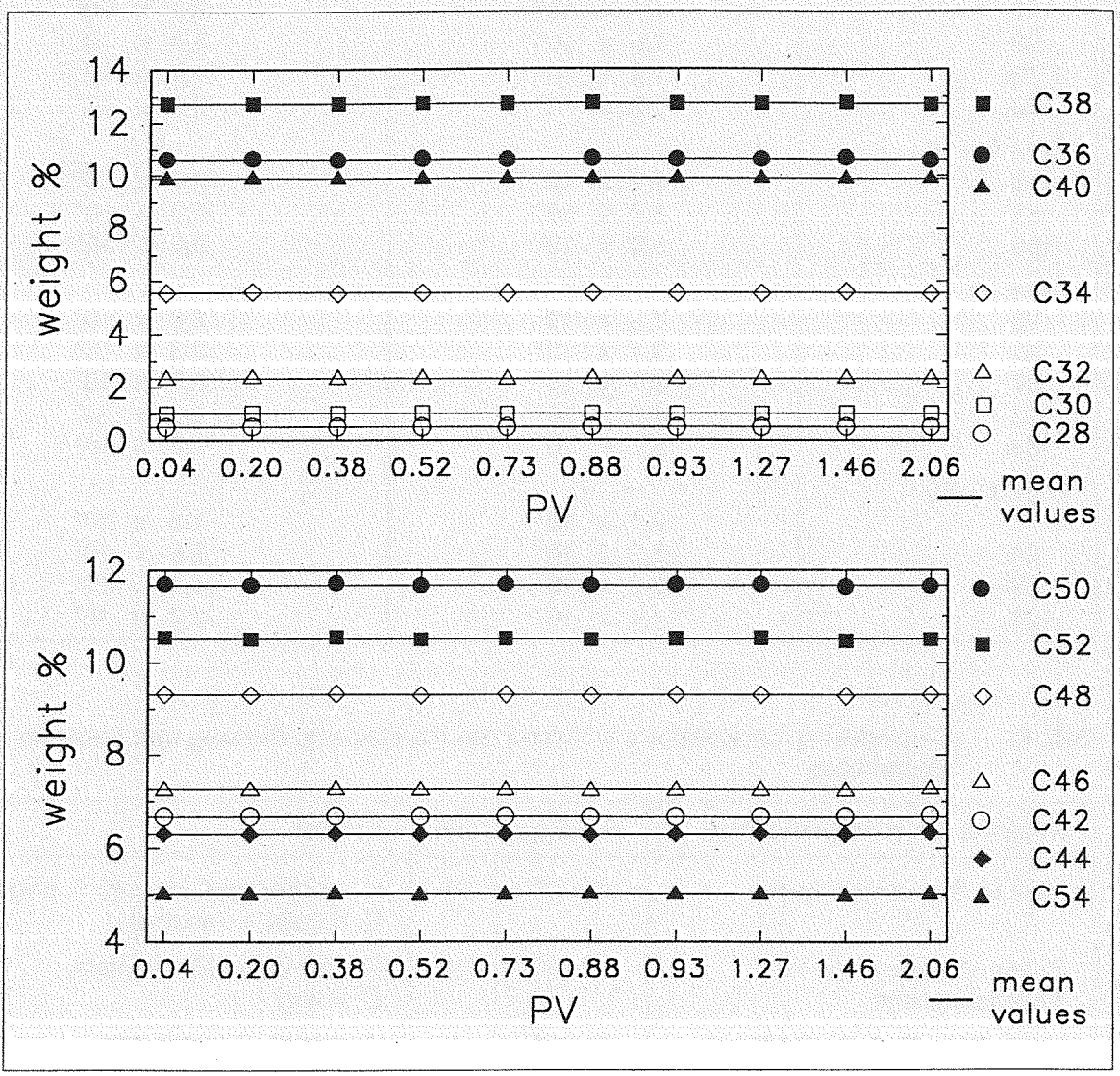

Fig. 6: Triglyceride contents of a transition period milk fat with rising PV

material, i.e. the accuracy of measurement. Since SD_1 values are only slightly higher than SD_2 values and there is no temporal tendency in percent values, autoxidation has no perceptible effect on triglyceride contents within the investigated PV range. So foreign fat detection by quantitative triglyceride analysis (8, 9) is even practicable with aged milk fats.

Tab. 1: Triglyceride contents (wt. %) of a winter period milk fat with rising PV

Time PV	0 h 0.19	1 h 0.38	2 h 0.55	3 h 0.70	4 h 0.89	5 h 1.06	6 h 1.25	7 h 1.32	24 h 1.52	48 h 2.22	Mean	SD_1 (0-48 h)	SD_2 (9x0 h)
Chol	0.33	0.32	0.32	0.32	0.31	0.32	0.32	0.32	0.33	0.32	0.32	0.006	0.006
C24	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.000	0.000
C26	0.23	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.23	0.22	0.004	0.005
C28	0.58	0.57	0.56	0.57	0.56	0.58	0.57	0.57	0.57	0.58	0.57	0.007	0.005
C30	1.17	1.14	1.15	1.14	1.14	1.16	1.15	1.16	1.15	1.16	1.15	0.010	0.005
C32	2.66	2.62	2.62	2.61	2.61	2.64	2.65	2.64	2.64	2.65	2.63	0.018	0.008
C34	6.26	6.18	6.18	6.18	6.17	6.22	6.20	6.21	6.21	6.22	6.20	0.027	0.018
C36	11.60	11.53	11.54	11.60	11.54	11.63	11.52	11.56	11.57	11.57	11.57	0.035	0.026
C38	13.00	12.96	12.97	13.04	12.98	13.06	12.94	12.99	12.99	12.97	12.99	0.036	0.021
C40	9.70	9.70	9.71	9.72	9.71	9.72	9.69	9.71	9.71	9.71	9.71	0.009	0.010
C42	7.26	7.28	7.30	7.26	7.29	7.24	7.29	7.27	7.27	7.28	7.27	0.018	0.006
C44	7.05	7.07	7.07	7.03	7.08	7.01	7.09	7.05	7.06	7.09	7.06	0.026	0.009
C46	7.78	7.82	7.81	7.79	7.82	7.76	7.81	7.78	7.79	7.79	7.79	0.020	0.011
C48	9.36	9.41	9.40	9.43	9.42	9.39	9.40	9.38	9.39	9.37	9.39	0.022	0.015
C50	10.83	10.90	10.89	10.94	10.90	10.90	10.86	10.89	10.87	10.85	10.88	0.031	0.024
C52	8.73	8.79	8.78	8.79	8.79	8.78	8.77	8.78	8.76	8.74	8.77	0.021	0.019
C54	3.46	3.50	3.49	3.40	3.47	3.39	3.52	3.48	3.47	3.47	3.46	0.041	0.010

Tab. 2: Triglyceride contents (wt. %) of a transition period milk fat with rising PV

Time PV	0 h 0.04	1 h 0.20	2 h 0.38	3 h 0.52	4 h 0.73	5 h 0.88	6 h 0.93	7 h 1.27	24 h 1.46	48 h 2.06	Mean	SD_1 (0-48 h)	SD_2 (9x0 h)
Chol	0.33	0.34	0.33	0.34	0.34	0.34	0.33	0.32	0.34	0.33	0.33	0.007	0.000
C24	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.000	0.000
C26	0.21	0.21	0.21	0.21	0.21	0.21	0.21	0.21	0.21	0.22	0.21	0.003	0.000
C28	0.53	0.54	0.53	0.53	0.53	0.54	0.53	0.53	0.54	0.54	0.53	0.005	0.000
C30	1.03	1.04	1.03	1.04	1.03	1.04	1.03	1.03	1.04	1.05	1.04	0.007	0.000
C32	2.33	2.36	2.32	2.35	2.33	2.35	2.34	2.33	2.36	2.35	2.34	0.014	0.011
C34	5.56	5.59	5.53	5.58	5.56	5.58	5.56	5.55	5.61	5.55	5.57	0.023	0.022
C36	10.61	10.63	10.59	10.64	10.61	10.64	10.61	10.60	10.67	10.58	10.62	0.027	0.026
C38	12.73	12.74	12.73	12.75	12.73	12.76	12.73	12.73	12.78	12.70	12.74	0.021	0.013
C40	9.87	9.88	9.88	9.88	9.88	9.89	9.88	9.88	9.89	9.88	9.88	0.006	0.007
C42	6.67	6.67	6.68	6.67	6.67	6.66	6.67	6.68	6.67	6.70	6.67	0.011	0.013
C44	6.31	6.30	6.31	6.30	6.31	6.28	6.31	6.32	6.30	6.34	6.31	0.015	0.011
C46	7.25	7.24	7.26	7.24	7.25	7.23	7.25	7.25	7.23	7.27	7.25	0.013	0.009
C48	9.31	9.29	9.32	9.29	9.31	9.28	9.30	9.30	9.27	9.30	9.30	0.015	0.012
C50	11.70	11.67	11.72	11.67	11.70	11.67	11.69	11.69	11.64	11.66	11.68	0.023	0.013
C52	10.54	10.50	10.55	10.50	10.52	10.50	10.52	10.53	10.47	10.50	10.51	0.024	0.016
C54	5.03	5.02	5.04	5.01	5.02	5.03	5.03	5.04	4.99	5.04	5.03	0.016	0.012

The effect of rising peroxide values on fatty acid composition of the same two milk fats is to be seen in Tab. 3 and 4. As no temporal tendency is indicated and the standard deviations SD_1 and SD_2 calculated for the main fatty acids are nearly the same, there is no change in fatty acid contents within the considered PV range. The significant constancy of fatty acid composition is also shown in Fig. 7 and 8.

A theoretical calculation of the presumable effect of autoxidation on milk fat composition confirms that there are no perceptible changes to be expected in triglyceride contents

Tab. 3: Fatty acid composition (wt. %) of a winter period milk fat with rising PV

Time PV	0 h 0.19	1 h 0.38	2 h 0.55	3 h 0.70	4 h 0.89	5 h 1.06	6 h 1.25	7 h 1.32	24 h 1.52	48 h 2.22	Mean	SD_1 (0-48 h)	SD_2 (5x0 h)
C4	3.95	4.09	4.01	3.99	3.96	3.87	4.02	3.91	3.96	4.00	3.98	0.061	0.060
C5	0.03	0.04	0.03	0.03	0.04	0.03	0.03	0.03	0.04	0.04			
C6	2.41	2.44	2.41	2.40	2.37	2.41	2.41	2.36	2.37	2.39	2.40	0.025	0.032
C7	0.03	0.03	0.04	0.03	0.04	0.04	0.04	0.03	0.03	0.02			
C8	1.40	1.41	1.39	1.38	1.38	1.41	1.41	1.36	1.37	1.39	1.39	0.018	0.027
C9	0.04	0.04	0.04	0.04	0.03	0.04	0.06	0.03	0.05	0.03			
C10	3.05	3.14	3.13	3.10	3.09	3.07	3.08	3.00	3.02	3.03	3.07	0.046	0.048
C10:1	0.30	0.30	0.29	0.30	0.29	0.30	0.30	0.29	0.29	0.30			
C11	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05			
C12	3.82	3.86	3.83	3.80	3.81	3.87	3.82	3.75	3.77	3.78	3.81	0.038	0.040
C12:1	0.10	0.11	0.10	0.09	0.10	0.10	0.10	0.10	0.10	0.09			
C13 iso	0.03	0.03	0.04	0.02	0.02	0.03	0.02	0.02	0.03	0.03			
C13 aiso	0.08	0.09	0.09	0.08	0.08	0.09	0.08	0.08	0.09	0.08			
C13	0.09	0.11	0.09	0.09	0.09	0.09	0.10	0.09	0.09	0.09			
C14 iso	0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.12	0.10			
C14	11.55	11.61	11.57	11.51	11.54	11.67	11.52	11.41	11.51	11.50	11.54	0.070	0.070
C14:1	1.02	1.03	1.02	1.02	1.02	1.04	1.04	1.02	1.02	1.03			
C15 iso	0.26	0.27	0.26	0.27	0.26	0.29	0.30	0.26	0.25	0.26			
C15 aiso	0.47	0.48	0.47	0.48	0.48	0.49	0.51	0.47	0.47	0.48			
C15	1.09	1.09	1.08	1.08	1.09	1.11	1.09	1.08	1.08	1.10			
C16 iso	0.23	0.24	0.24	0.25	0.24	0.24	0.25	0.24	0.23	0.24			
C16	31.89	31.69	31.44	31.58	31.60	31.75	31.63	31.65	31.84	31.68	31.68	0.130	0.096
C16:1	1.96	1.95	1.95	1.96	1.95	1.98	1.98	1.98	1.97	1.97			
C17 iso	0.37	0.37	0.38	0.38	0.37	0.38	0.40	0.38	0.37	0.38			
C17	0.54	0.54	0.54	0.56	0.54	0.55	0.58	0.58	0.55	0.56			
C17:1	0.22	0.23	0.24	0.24	0.24	0.23	0.23	0.24	0.23	0.23			
C18 iso	0.06	0.07	0.08	0.08	0.08	0.07	0.08	0.08	0.08	0.08			
C18	9.48	9.37	9.30	9.39	9.42	9.32	9.34	9.53	9.43	9.39	9.40	0.071	0.054
C18:1*)	20.75	20.56	20.48	20.69	20.74	20.58	20.53	21.00	20.78	20.61	20.67	0.154	0.174
C18:2*)	1.59	1.59	1.64	1.66	1.67	1.63	1.61	1.67	1.65	1.61			
C18:3	0.40	0.40	0.42	0.42	0.42	0.41	0.40	0.43	0.42	0.40			
C18:2conj.	0.35	0.36	0.39	0.37	0.38	0.37	0.35	0.39	0.37	0.36			
C19	0.18	0.18	0.20	0.20	0.20	0.19	0.19	0.20	0.20	0.20			
C19:2	0.11	0.12	0.15	0.14	0.14	0.13	0.12	0.14	0.13	0.14			
C20	0.14	0.15	0.18	0.17	0.17	0.15	0.14	0.16	0.16	0.16			
C20:3	0.04	0.05	0.06	0.06	0.06	0.06	0.04	0.06	0.05	0.06			
C20:4	0.08	0.08	0.09	0.08	0.08	0.08	0.08	0.09	0.08	0.08			
C21	0	0.02	0.03	0.03	0.03	0.02	0.02	0.02	0.02	0.03			
C22	0.05	0.05	0.07	0.06	0.05	0.05	0.06	0.06	0.06	0.06			
Total	98.32	98.35	97.93	98.19	98.23	98.30	98.12	98.35	98.33	98.03			
Rest	1.68	1.65	2.07	1.81	1.77	1.70	1.88	1.65	1.67	1.87			

*) including all isomeres

and fatty acid composition up to peroxide values of 10. Even higher PVs will not implicitly affect e. g. the performance of foreign fat detection in milk fat by triglyceride analysis.

For investigating the dependence of autoxidation upon light a milk fat from the summer period with a higher content of unsaturated fatty acids was used. Preparation of the samples was performed as described for the preceding measurements. Afterwards opened glasses with milk fat were kept in an airated, dark oven at two different temperatures, 22°C and 50°C. In Tab. 5 peroxide values for different times of air exposure are given. At 22°C storage temperature changes in PV lie in the range of detection accuracy and can be neglected. Even at 50°C a perceptible increase is not found before a reaction time of 48 h. Compared with the distinct increase of peroxide value for a milk fat stored at room temperature under daylight (Tab.1 and 2), autoxidation is rather slow in the dark even for a fat with higher iodine value.

Tab. 4: Fatty acid composition (wt. %) of a transition period milk fat with rising PV

Time PV	0 h 0.04	1 h 0.20	2 h 0.38	3 h 0.52	4 h 0.73	5 h 0.88	6 h 0.93	7 h 1.27	24 h 1.46	48 h 2.06	Mean	SD_1 (0-48 h)	SD_2 (5x0 h)
C4	3.96	3.97	3.92	4.02	3.97	3.84	3.94	3.90	3.90	3.91	3.93	0.050	0.060
C5	0.03	0.02	0.02	0.03	0.02	0.02	0.02	0.02	0.02	0.02			
C6	2.28	2.26	2.25	2.29	2.28	2.28	2.23	2.23	2.24	2.25	2.26	0.022	0.032
C7	0.03	0.03	0.04	0.02	0.02	0.03	0.02	0.04	0.03	0.02			
C8	1.28	1.29	1.26	1.29	1.27	1.27	1.29	1.28	1.29	1.25	1.28	0.014	0.027
C9	0.03	0.03	0.03	0.02	0.04	0.04	0.04	0.02	0.03	0.03			
C10	2.69	2.69	2.66	2.74	2.71	2.70	2.68	2.64	2.67	2.65	2.68	0.030	0.048
C10:1	0.28	0.29	0.27	0.27	0.27	0.28	0.27	0.27	0.27	0.27			
C11	0.04	0.07	0.03	0.03	0.03	0.03	0.04	0.03	0.03	0.03			
C12	3.29	3.34	3.29	3.35	3.38	3.36	3.29	3.26	3.32	3.29	3.32	0.039	0.040
C12:1	0.08	0.09	0.09	0.09	0.08	0.08	0.08	0.08	0.08	0.08			
C13 iso	0.04	0.04	0.05	0.04	0.04	0.04	0.04	0.04	0.04	0.04			
C13 aiso	0.08	0.08	0.08	0.08	0.07	0.08	0.08	0.08	0.08	0.08			
C13	0.07	0.08	0.08	0.08	0.08	0.08	0.07	0.08	0.08	0.08			
C14 iso	0.14	0.16	0.14	0.15	0.14	0.14	0.13	0.14	0.14	0.14			
C14	10.69	10.71	10.64	10.80	10.74	10.81	10.62	10.54	10.78	10.66	10.70	0.087	0.070
C14:1	0.97	0.98	0.98	0.98	0.97	0.98	0.96	0.95	0.98	0.97			
C15 iso	0.33	0.34	0.35	0.34	0.33	0.34	0.34	0.33	0.33	0.33			
C15 aiso	0.58	0.59	0.60	0.59	0.58	0.59	0.59	0.58	0.58	0.58			
C15	1.12	1.13	1.14	1.13	1.13	1.14	1.12	1.11	1.13	1.12			
C16 iso	0.26	0.26	0.27	0.26	0.27	0.27	0.27	0.26	0.26	0.27			
C16	27.93	27.55	27.88	27.97	27.96	28.08	27.84	27.80	28.11	27.99	27.91	0.160	0.096
C16:1	1.93	1.93	1.94	1.92	1.92	1.93	1.92	1.93	1.95	1.93			
C17 iso	0.41	0.51	0.41	0.41	0.41	0.41	0.41	0.41	0.41	0.50			
C17	0.59	0.59	0.62	0.58	0.59	0.59	0.59	0.60	0.60	0.59			
C17:1	0.25	0.27	0.27	0.24	0.24	0.25	0.25	0.26	0.26	0.25			
C18 iso	0.08	0.10	0.09	0.07	0.07	0.08	0.08	0.08	0.08	0.08			
C18	10.57	10.31	10.60	10.47	10.55	10.46	10.57	10.63	10.44	10.66	10.53	0.106	0.054
C18:1*)	24.11	23.56	23.81	23.92	23.87	23.97	24.12	24.34	24.10	24.15	24.00	0.218	0.174
C18:2*)	1.72	1.80	1.76	1.70	1.66	1.73	1.75	1.79	1.74	1.76			
C18:3	0.47	0.48	0.49	0.47	0.48	0.48	0.48	0.50	0.49	0.49			
C18:2conj.	0.68	0.68	0.71	0.68	0.70	0.68	0.70	0.73	0.71	0.71			
C19	0.24	0.26	0.24	0.23	0.21	0.24	0.24	0.25	0.24	0.24			
C19:2	0.16	0.19	0.17	0.16	0.14	0.17	0.17	0.17	0.16	0.18			
C20	0.19	0.20	0.19	0.18	0.21	0.18	0.19	0.21	0.17	0.20			
C20:3	0.05	0.06	0.04	0.05	0.09	0.05	0.06	0.06	0.06	0.06			
C20:4	0.07	0.07	0.07	0.07	0.09	0.07	0.08	0.08	0.08	0.08			
C21	0.03	0.05	0.03	0.03	0.03	0.03	0.03	0.04	0.03	0.04			
C22	0.07	0.08	0.07	0.07	0.08	0.06	0.08	0.08	0.08	0.08			
Total	97.82	97.14	97.58	97.82	97.92	97.86	97.68	97.84	97.99	98.06			
Rest	2.18	2.86	2.42	2.18	2.08	2.14	2.32	2.16	2.01	2.94			

*) including all isomeres

Tab. 5: Changes in PV by autoxidation in the dark for a summer period milk fat

reaction time (h)	stored at 22 °C	stored at 50 °C
0	0.06	0.06
1	0.07	0.06
2	0.06	0.07
3	0.07	0.08
4	0.07	0.07
5	0.08	0.07
6	0.07	0.08
7	0.07	0.07
24	0.08	0.08
48	0.08	0.14

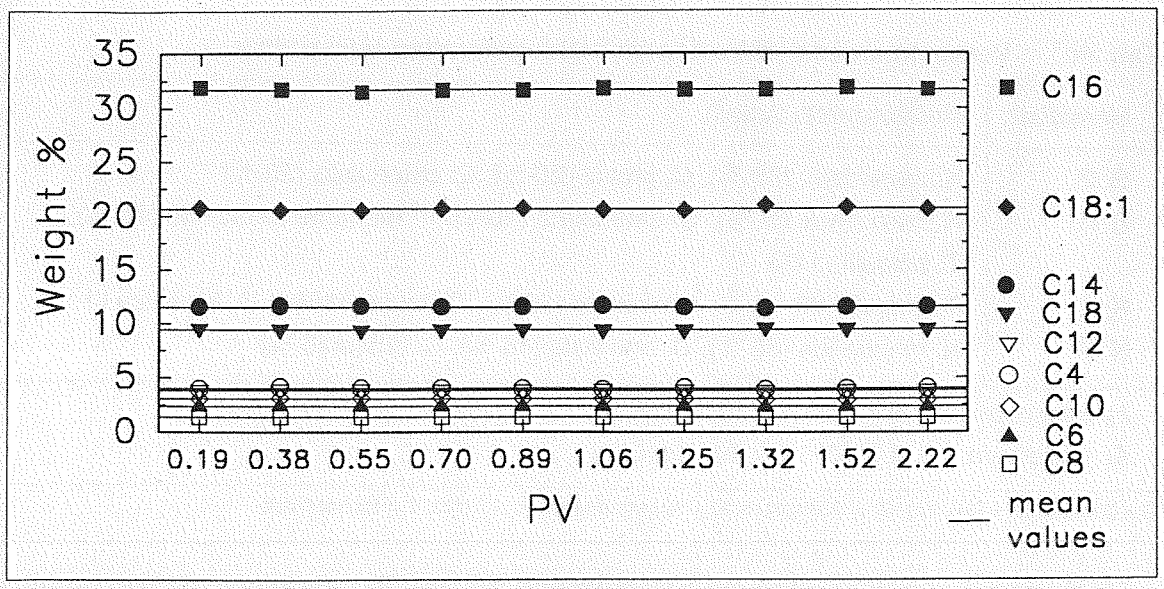

Fig. 7: Fatty acid composition of a winter period milk fat with rising PV

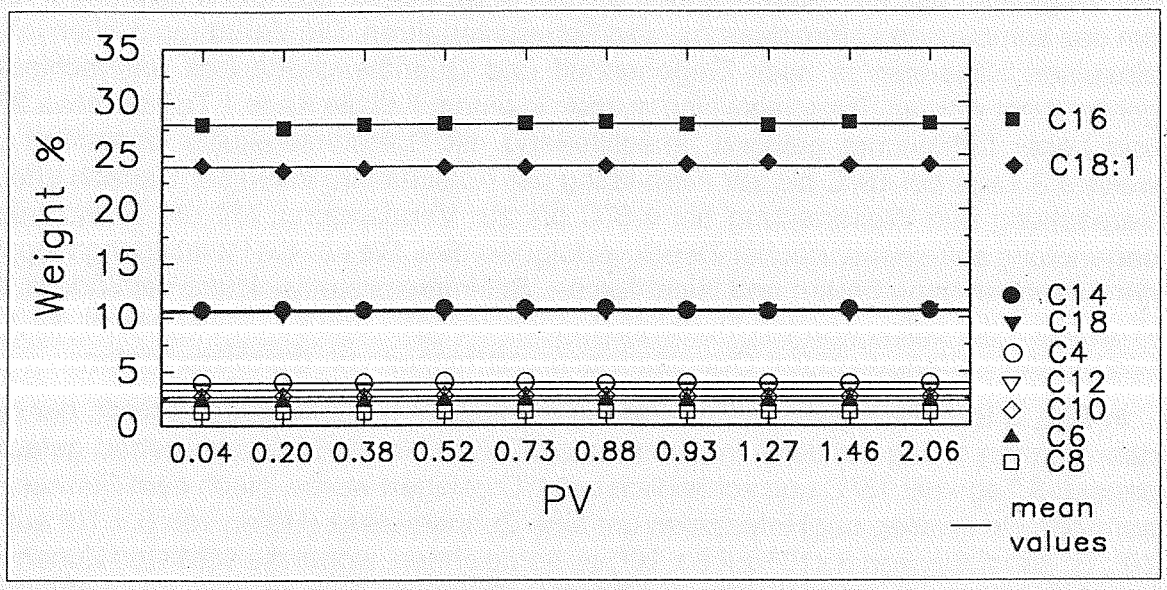

Fig. 8: Fatty acid composition of a transition period milk fat with rising PV

So long-term storage of fat samples without any perceptible changes in fat parameters is possible if in addition to an oxygen-free atmosphere and deep temperatures exclusion of light is guaranteed.

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5. Summary

Molkentin, J., Precht, D.: **The influence of autoxidation on milk fat composition.** Kieler Milchwirtschaftliche Forschungsberichte **45** (4) 373–383 (1993)

44 Milk fat (autoxidation, stability, composition)

The influence of autoxidation processes upon milk fat composition is described. Time resolved changes in peroxide value (PV), ultraviolet absorbance, triglyceride contents and fatty acid composition are shown. Changes in PV and UV absorbance are compared and the great influence of light on autoxidation is demonstrated.

Within the investigated PV range of about 0 to 2 no perceptible changes in triglyceride and fatty acid contents were found with respect to accuracy of measurements. The rises in PV and UV absorbance cannot be correlated directly even for a single fat, but both parameters are increasing after an initial period. Exclusion of light nearly leads to inertness against autoxidation even at a temperature of 50°C.

Long-term storage of milk fats will not affect milk fat parameters if samples are kept under nitrogen at -18°C in the dark. So application of a milk fat reference material over a longer period is possible. Even beginning autoxidation will not implicitly affect e. g. the performance of foreign fat detection in milk fat by triglyceride analysis.

Zusammenfassung

Molkentin, J., Precht, D.: **Zum Einfluß der Autoxidation auf die Milchfettzusammensetzung.** Kieler Milchwirtschaftliche Forschungsberichte **45** (4) 373–383 (1993)

45 Milchfett (Autoxidation, Stabilität, Zusammensetzung)

Der Einfluß von Autoxidationsprozessen auf die Zusammensetzung von Milchfett wird beschrieben. Zeitaufgelöste Veränderungen der Peroxidzahl (POZ), der UV-Absorption, der Triglyceridgehalte und der Fettsäurenzusammensetzung werden aufgezeigt. Veränderungen der POZ und der UV-Absorption werden gegenübergestellt und der starke Einfluß von Licht auf die Autoxidation wird verdeutlicht.

Innerhalb des untersuchten POZ-Bereiches von etwa 0 bis 2 wurden keine im Rahmen der Meßgenauigkeit wahrnehmbaren Veränderungen der Triglycerid- und Fett-

säurenzusammensetzung festgestellt. Die zeitlichen Verläufe von POZ und UV-Absorption können weder zwischen verschiedenen Milchfetten, noch für ein einzelnes Milchfett direkt korreliert werden. Allerdings steigen beide Parameter nach einer Anfangsperiode an. Der Ausschluß von Licht führt sogar bei Temperaturen von 50°C zur nahezu vollständigen Resistenz gegen die Autoxidation.

Bei einer Langzeitlagerung von Milchfetten unter Stickstoff bei -18°C im Dunkeln werden die Milchfettparameter folglich nicht beeinflußt. Damit ist die Anwendung von Referenzmilchfetten über einen längeren Zeitraum möglich. Selbst eine beginnende Autoxidation wird z.B. die Durchführung der Fremdfettbestimmung in Milchfett durch Triglyceridanalytik nicht beeinflussen.

Résumé

Molkentin, J., Precht, D.: **L'influence de l'autoxydation sur la composition de la matière grasse laitière.** Kieler Milchwirtschaftliche Forschungsberichte **45** (4) 373–383 (1993)

44 Matière grasse laitière (autoxydation, stabilité, composition)

On décrit l'influence des procédés d'autoxydation sur la composition de la matière grasse laitière. On montre des changements, résolus en fonction du temps, de la valeur de peroxyde (VP), de l'absorption U.V., des teneurs en triglycérides et de la composition d'acides gras. On compare des changements de la VP et de l'absorption U.V. et on démontre la grande influence de la lumière sur l'autoxydation.

Au-dedans de la portée VP étudiée, étant d'env. 0 à 2, on n'a pas observé des changements des teneurs en triglycérides et en acides gras perceptibles dans le cadre de la précision du mesurage. Les variations temporelles de l'absorption VP et U.V. ne peuvent être corrélées directement, ni entre des matières grasses laitières différentes, ni pour une matière grasse laitière individuelle; d'autre part, les deux paramètres vont en augmentant après une période initiale. L'exclusion de la lumière aboutit à une résistance presque complète à l'autoxydation même à des températures de 50°C.

Le stockage à long terme de matières grasses laitières ne produit, donc, aucun effet sur les paramètres de la matière grasse laitière, si les échantillons sont conservés sous l'azote à -18°C dans l'ombre. Par conséquent, l'application de matières grasses laitières de référence est possible pendant une période prolongée. Même une autoxydation commençante n'affectera pas, e.g, la détermination de graisses étrangères dans la matière grasse du lait à l'aide de l'analyse de triglycérides.