Thermogravimetric analysis (TGA) of different hog and cattle tissue lipids

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SUMMARY: The rate of volatile compound formation from lipids extracted from various different hog and cattle tissues (muscle and fatty tissues, spinal cord, brain and liver) was investigated by thermogravimetric analysis.

The obtained results show that the rate of volatile formation decreased in the following series: liver, muscle tissue, brain, spinal cord and fatty tissue. The total quantity of volatile compounds was always about 20% larger in the case of samples extracted from hog tissue as compared to the corresponding samples from cattle tissues. Comparison of TGA results obtained in air (oxidizing atmosphere) with those obtained in nitrogen, all other operating conditions being the same, indicated that lipids extracted from muscle tissue, the liver and the spinal cord showed the largest reactivity to oxygen.

Experimental results were interpreted using data on mass change occuring above 130°. The rate of volatile compound formation was analysed using a first order kinetic expression. Activation energies in the range 14-55 kJ/mol were determined. A simple correlation between the observed activation energy and the phospholipid content of the sample was observed.

INTRODUCTION: As was recently shown by Lj. Bastić et al. (1987), the rate of volatile compound formation can be determined using non-isothermal thermogravimetric procedures. Moreover, the same authors also used differential scanning calorimetry (DSC) to show that very simple correlations exist between the heat of fusion or the total heat effects of oxidation and the lipids composition (Skala et al.,1989, 1990). TGA and DSC have been successfully applied to determine various characteristics of natural substances (application of DSC analysis: Le Meste et al., 1984; Tiunova, 1988; Schlichter, 1988; Garti et al., 1988; application of TGA: Cross, 1970). The results obtained indicated that fusion effects of the total lipids can be correlated to their composition, esspecially to the concentration of polyunsaturated and monounsaturated acids in the total lipids (Skala et al., 1989). the different composition of the total lipids obtained from hog and cattle tissues also influences the total exothermal heat effect of lipid oxidation. Thus, a simple relation was derived between the heat of oxidation, as determined by DSC, and the total content of unsaturated (poly- and mono-) fatty acids present in the total lipids (Skala et al., 1990). Taking into account the results of TGA performed using Boar *M. Semimembranosus* intramuscular lipids (Lj. Bastić et al., 1987),and a suggestion that such an analysis could serve as a standard procedure for the rate of volatile compounds determination, the main task of the present study was to show that TGA analysis could serve as a powerful tool for the fast detection of the difference in total lipids origin and for correlating the main kinetic parameters of oxidation processes to the total lipids composition. TGA also yields some additional information about the thermal and oxidation stability of total lipids extracted from different hog and cattle tissues which is of interest in determining changes in the composition of meat during different thermal processes (pasteurization or sterilization).

MATERIALS AND METHODS: The preparation of samples of total lipids from different hog and cattle tissues is given in detail in the paper of M. Bastić et al. (1989). TG analysis in air and nitrogen as carrier gas was performed using lipid samples held at 4°C for 2.5 years after their preparation. The total lipids from muscle and fatty tissues were fractionated to neutral lipids, glucolipids and phospholipids by Johnston's procedure (1983). The sample of neutral lipids from hog fatty tissues was further separated and the obtained fraction of triglycerides was analysed using the same TGA procedure.

TGA investigations in oxidizing and inert atmosphere were performed using a Perkin Elmer TGS-2 system. The heating rate of the sample was 2.5-10 K/min in the temperature range 30-230°C, while the carrier flow rate was always held constant, 28 cm^3/min.All the investigations were performed with approximately the same initial sample mass (7 mg).

The aim of using comparative TG analysis in air and nitrogen was to show that the different rates of volatile compounds formation are a consequence of the chemical reactions of oxidation which exist when a sample is heated in oxidizing atmosphere.

RESULTS AND DISCUSSION

Comparative analysis of TGA in air and nitrogen

Figures 1 and 2 present the cumulative mass changes of cattle intramuscular neutral lipids and lipids from the liver during heating to 230°C at 2.5, 5 and 10 K/min in air and nitrogen.

The presented TG curves indicate that the thermal degradation of volatile compounds formation is considerably increased at temperatures above 130°. The comparative results between mass changes in air and nitrogen for all the investigated samples are given in Table 1.

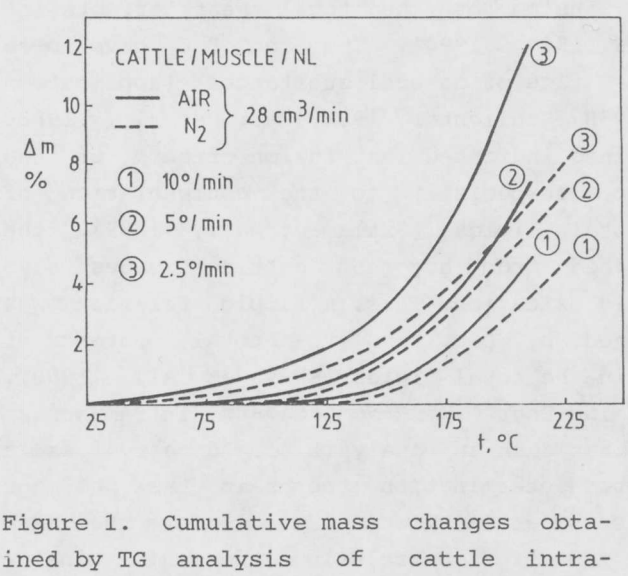

Figure 1. Cumulative mass changes obtained by TG analysis of cattle intramuscular neutral lipids at various heating rates in air and nitrogen carrier gas.

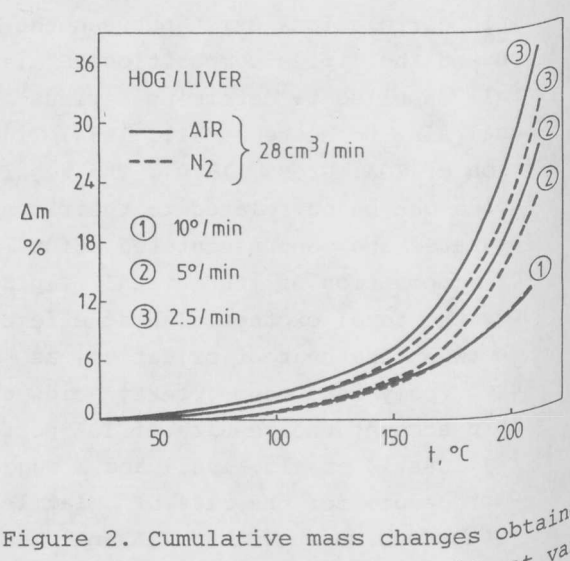

Figure 2. Cumulative mass changes obtained by TG analysis of hog liver lipids at various heating rates in air and nitrogen carrier gas.

Table 1. A difference in mass change when a sample was heated in air and nitrogen (symbols used: H=hog; C=cattle; M=muscle; L=liver; F= fatty; B= brain; SC= spinal cord; NL= neutral lipids; TG= triglycerides): $\Delta M = m_{200°} - m_{130°}$

Sample	air			nitrogen		
	2.5	5	10	2.5	5	10
	heating rate, K/min					
H - M	12.2	9.4	5.0	9.0	8.2	5.7
H - M/NL	-	-	2.5	-	-	2.1
H - L	22.5	15.6	8.2	19.0	14.1	8.5
H - F	-	-	0.1	0.3	-	0.1
H - F/NL	4.5	1.5	0.8	0.5	0.5	0.5
H - F/TG	-	3.1	2.3	-	-	1.8
H - SC	6.0	4.2	2.9	5.4	4.6	2.8
C - M/NL	8.0	4.9	3.6	4.5	4.2	2.6
C - L	19.6	13.0	6.0	17.2	11.1	5.8
C - F	2.6	-	0.2	0.5	-	0.1
C - F/NL	-	5.2	4.9	4.6	-	2.6
C - SC	4.8	2.9	1.8	5.2	4.4	3.2
C - B	8.1	6.4	4.0	7.9	6.7	4.6

The above values of mass change, determined by TGA, show that there is always about a 20% greater mass change for samples extracted from hog tissue, and that the mass change increases in a series of samples extracted from the liver, muscle tissue, brain, spinal cord, while the mass change for lipids extracted from fatty tissue is practically negligible. When comparing the mass changes in air and nitrogen atmosphere the greatest differences are found in the case of lipids extracted from muscle tissues, followed by the liver and spinal cord. With decreasing heating rate an increased quantity of volatile compounds was formed; quantitatively a 2 to 3 times greater mass change was observed when the heating rate was decreased from 10 to 2.5. The largest differences were obtained for total lipids extracted from the liver (C then H), muscle tissue and spinal cord.

The relative reactivity of samples to oxygen could be drawn by comparing the values of ΔM for the temperature interval 30°- 130° in air and nitrogen for different heating rates. There was also an increased value of ΔM but about 20-30% less in oxidizing atmosphere indicating that the formation of oxidizing products (peroxides) started at the beginning of thermal degradation processes which caused, in the latter stage, the formation of volatile compounds.

Determination of the kinetic parmeters for the rate of thermal degradation in the range 130° -200°C

Although a corresponding mass decrease is noted at temperatures below 130°C it is less intensive. That was the reason why only the mass change in the temperature interval 130°-200° was taken into account for determining the rate of volatile compounds formation (r_{VC}), using the same procedure explained in the paper of Lj. Bastić et al. (1987). It was defined by a simple kinetic expression valid for a first order reaction:

$$(r_{VC}) = -dM/dt = k(T).M$$

where k=A.exp(-E/RT), the apparent reaction rate constant which indicates the influence of temperature on the reacton rate of volatile compounds formation, i.e. the mass change of the investigated sample; M, is the actual sample mass at temperature T.
According to the procedure and method described by Doyle (1961) and Gorbachev (1975) the integral equation obtained from the above kinetic expression has a simple form which is of interest for determining kinetic parameters (A, frequency factor;, E, activation energy) and confirming the rate expression:

$$-\ln[-\ln(1-X)/T^2] = \ln(Z) + E/(R.T) \quad (1)$$

$$Z = A.R/[q.(E+2RT)] \quad ; \; q = K/min \quad \text{and} \quad R = 8.314 \; J/mol.K \quad (2)$$

The analysis of equation (1) is presented in Figure 3 for some of the samples investigated in the present study for q=2.5 K/min, while the determined kinetic parameters (A,E) from the corresponding slopes and the intercepts of the linear functions are presented in Table 2.

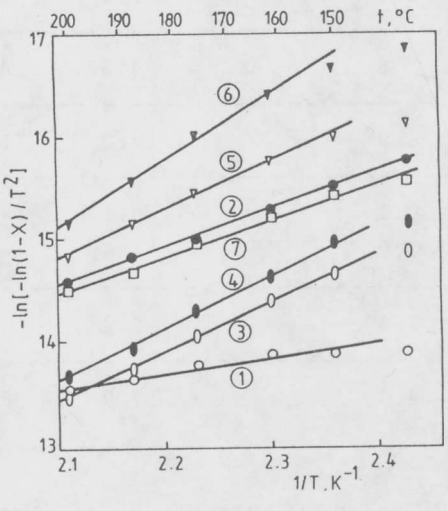

Figure 3. Analysis of equation (1) for q=2.5 K/min.(1-H/M ; 2-C/M/NL; 3-H/L; 4-C/L; 5-H/SC; 6-C/SC and, 7-C/B).

Table 2. Analysis of the slope and intercept of equation (1) for different heating rates (2.5, 5 and 10 K/min); symbols are the same as those used in Table 1. and calculated rate constants at 150 and 200°C.

Sample	phosph. (%)*	E, kJ/mol (average values)	A, min^{-1}	$k.10^3$ min^{-1} 200°	150°	k_H/k_C 200°	150°
H - M	24.4	14,700	0.319	7.59	4.88	2.4	1.4
H - L	64.2	43,000	1385.0	24.70	6.78	1.3	1.3
H - SC	56.6	40,700	157.5	5.04	1.48	4.3	2.9
C#- M/NL	22.8	31,600	16.5	5.34	2.07		
C - L	72.0	43,000	1100.4	19.62	5.39		
C - SC	71.4	55,000	2082.9	1.76	0.34		
C - B	58.4	31,600	18.2	5.89	2.28		

*according to Djordjević et al. (1987) and M. Bastić et al. (1989)
#presented data could not be used for the analysis (Fig.4) because it was obtained analysing only neutral fractions (C-M).

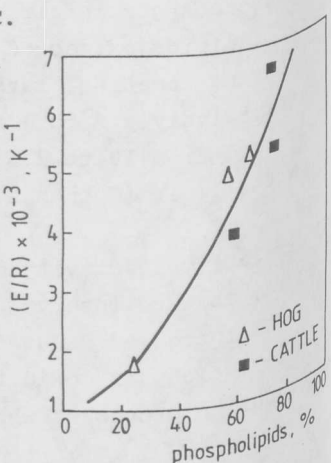

Figure 4. Activation energies *versus* phospholipid content

Looking at the results presented in Table 2., the activation energy of the rate of volatile compounds formation could be successfully correlated to the composition of total lipids, especially to the content of phospholipids. Such a correlation (Figure 4) is a very useful tool for the easy and fast identification of complex total lipids composition and the determination of volatile compounds formation.

CONCLUSION: The results of TG investigations performed in oxidizing and inert atmosphere indicated an increase in the mass change of samples heated above 130°. The rate of volatile formation for temeperatures greater than 130° was interpreted as a first order reaction and the corresponding kinetic parameters were determined using the standard Doyle-Gorbachev procedure. Quite a good relation between the activation energy of volatile compounds formation and the lipids composition was established using values of the content of phospholipids present in the total lipids.

The presented investigations, as well as the obtained results, show that TGA can be used as a practical method for the quantitative determination of volatile compounds which influence the formation of aromas of various materials and the content of phospholipids present in total lipids.

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