Changes in Egg Volatiles during Storage

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Abstract

ADAMIEC J., DOLEŽAL M., MÍKOVÁ K., DAVÍDEK J. (2002): **Changes in egg volatiles during storage**. Czech J. Food Sci., **20**: 79–82.

The quality of eggs is tightly associated with freshness. New possibilities for the determination of egg freshness were studied. The volatile compounds of eggs and their changes during storage were followed. Three methods for extraction of volatiles were compared: dynamic headspace (Purge and Trap), static headspace (Solid Phase of Microextraction – SPME) and extraction according to Likens-Nickerson by simultaneous distillation-extraction (SDE) with diethyl ether as organic solvent. The extracts were analysed by GC/FID. The volatiles in an extract obtained by SDE method were identified by GC-MS. The extract includes aldehydes, alcohols, acids and esters. The volatiles in an extract obtained by SPME and Purge and Trap have not been identified until now. The changes in volatiles during storage of eggs using the above mentioned methods were studied.

Keywords: quality of eggs; changes during storage; volatile compounds; Purge and Trap; Solid Phase of Microextraction; simultaneous distillation-extraction

Freshness of eggs is connected with quality. Quality of eggs is influenced by age and storage conditions (particularly temperature and relative humidity of the environment). The methods used for determination of quality are based on physical (e.g. air cell height measuring, pH measuring, refraction index, hydrometric method) and chemical (ROSSI *et al*. 1995; HILDAGO *et al*. 1995) (measuring of chemical substances, e.g. furosin, succinic acid, lactic acid, 2-hydroxybutyric acid) properties. In the present time the measurement of Haugh unit (HU) is used most frequently in commercial practice. The HU results from the weight of shell egg (W) and the height of egg thick white (H). It is defined by the mathematical relationship (NARUSHIN 1997):

$$HU = 100 \times \log (H - 1.7 \times W^{0.37} + 7.6)$$

The higher value of HU corresponds to the better quality of eggs if other characteristic are good.

A number of studies on egg volatiles have been reported, but in most cases the eggs were either boiled before analysis or were heated during the process of volatiles extraction or analysis. MACLEOD and CAVE (1975) studied a suitable method for preparation of samples for an analysis of volatiles. Finally they used a simultaneous steam distillation-solvent extraction in modified Likens-Nickerson apparatus. UMANO *et al.* (1990) determined 141 volatile components in cooked whole eggs, egg yolk and egg white. According to them whole eggs contain nitriles, alkylbenzenes, ketones, pyrazines, pyrroles and pyridines as major components. Cooked egg yolk contains large numbers of aldehydes and pyrazines while the major components of cooked egg white are ketones, pyrazines and nitriles. SATO *et al*. (1973) identified amines, alcohols, aldehydes and ketones in the volatiles from unheated, fresh egg whites.

BROWN *et al.* (1986) described the volatile indicators of deterioration in uncooked eggs. They observed the accumulation of compounds as dimethyl sulfide, dimethyl disulfide, dimethyl trisulfide, methyl thioacetate, methanol, ethanol, 1-propanol, acetone, 2-butanone and ethyl acetate.

MATERIAL AND METHODS

Material. The eggs of Lohmann hen hybrid line from cages were stored 0–12 days at 35°C. One day of this

Supported by Research Project No. 525/99/0528 granted by Grant Agency of the Czech Republic.

storage of eggs corresponds approximately to three days of storage under ambient conditions. The eggs were analysed at the beginning of storage experiment and then on the fourth, seventh, and twelfth day of storage. Together with determination of volatiles, HU values were determined using TSS EQS apparatus.

After breaking of eggs, egg yolks were separated from egg whites and only yolks were used for the following analysis.

Purge and Trap. The trap Vocarb™ 3000 (Carbopack B/Carboxen) was chosen for adsorption. 30 g of yolks were weighted to the flask and homogenised with 50 ml of saturated solution NaCl. The sorption was carried out over 30 min in dynamic headspace. All work was carried out in inert atmosphere.

Solid phase of microextraction. For adsorption of egg yolk volatiles the fiber PDMS/DVB (Polydimehylsiloxane/Divinylbenzene) of thickness 65 µm was chosen.

30 g of homogenized yolks were weighted to a vial. The sorption was carried over 60 min in headspace at 40°C.

Simultaneous distillation-extraction (SDE). 75 g of homogenized yolks were weighted and blended with 0.5 l water. The flask was connected to modified Likens-Nickerson apparatus heated to boiling point, boiled 60 min and volatiles were extracted into 100 ml diethyl ether. The extract was evaporated to 200 µl. 1-pentanol was used as inside standard.

Gas chromatography (GC). The gas chromatograph was a Hewlett-Packard 6890 Plus with flame ionization detector (FID) and with column HP-INNOWAX, 30m × 0.25 mm × 0.25 µm. The helium carrier gas flow rate was 1 ml/min. The oven temperature was maintained at 40°C for 3 min. after which the temperature was programmed to 240°C at 3°C/min. Detector and injector temperatures were 250°C, only the temperature at SDE injector was 220°C.

Gas chromatography-Mass spectrometry (GC-MS). The gas chromatograph Hewlett-Packard G1800 A with quadrupole mass spectrometer (MS) was used for identification of compounds. The helium carrier gas flow rate was 1ml/min. The volatiles obtained by Purge and Trap and SPME were not identified.

RESULTS AND DISCUSSION

Although the volatiles obtained by the methods Purge and Trap and SPME have not been identified until now, the changes in areas of selected peaks were monitored during storage in the above described conditions. The chromatogram obtained by an analysis of the extract of Purge and Trap is shown in Fig. 1 and chromatogram obtained by SPME in Fig. 2. Changes in peak areas of volatiles during ageing of eggs are given in Table 1 for Purge and Trap and in Table 2 for SPME method.

The changes in peak areas obtained by SPME method show that the concentrations of volatiles of unheated yolks decreased during storage time. The changes in selected peak areas obtained by Purge and Trap method had mostly an increasing trend. The biggest changes were at the beginning of experiment. Fresh eggs have a very low concentration of volatiles and this concentration escalates during storage. The area of some peaks is decreasing during the time of storage, obviously some volatiles escape through the shell or participate in reactions with other components of eggs.

Table 1. Changes in peak areas of volatiles in extract obtained by Purge and Trap method

Peak No.	Days of storage			
	0	4	7	12
1	200	1202	1708	2166
2	9	66	57	102
3	12	170	802	69
4	50	121	90	83
5	178	684	1111	1149
6	43	143	144	279
7	18	173	43	33
8	6	60	54	59
9	3	50	51	51

See Fig. 1

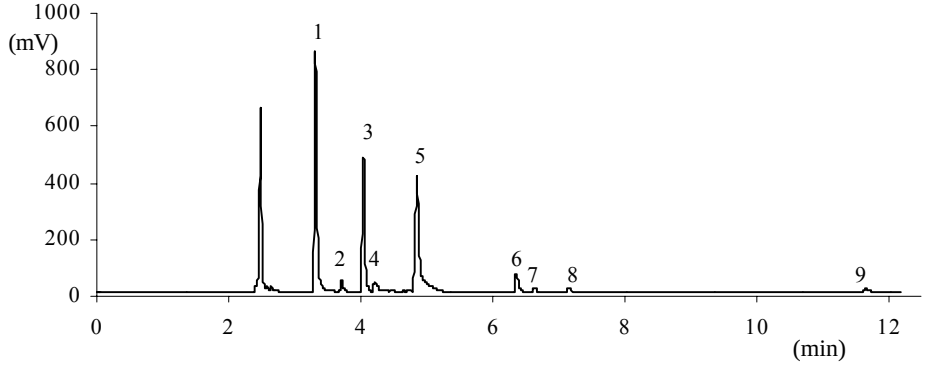

Fig. 1. Chromatogram of volatiles in extract obtained by Purge and Trap method

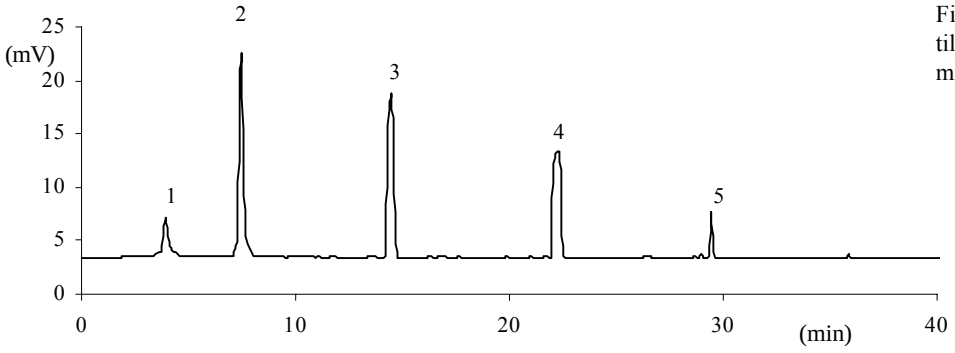

Fig. 2. Chromatogram of volatiles in extract obtained by SPME method

Table 2. Changes in peak areas of volatiles in extract obtained by SPME method

Peak No.	Days of storage			
	0	4	7	12
1	87	61	55	39
2	330	223	205	177
3	303	135	133	111
4	223	55	58	41
5	39	8	10	5

See Fig. 2

The differences between SPME and Purge and Trap method can be explained by a higher temperature used in SPME method. It indicates the loss of volatiles at this condition. The sensitivity of Purge and Trap method was significantly higher than in SPME method.

The changes in HU values are given in Table 3. As we supposed, the HU values decreased during storage.

Table 3. Changes in HU values during storage

Days of storage	0	4	7	12
Haugh units	77	56	42	35

Using modified Likens-Nickerson apparatus (SDE method) 48 substances were identified. From them six substances (present in the highest concentration) were chosen for further experiments. The chromatogram obtained by an analysis of SDE extract is shown in Fig. 3. The concentration changes in volatiles during ageing of eggs are shown in Table 4.

It is obvious that the changes in individual compounds were different. An increasing trend was observed in palmitic and stearic acids, most probably as a result of lipid hydrolysis. The changes in other substances fluctuate during the storage time of eggs.

The best method for the determination of egg volatiles was proved to be Purge and Trap procedure because this

Table 4. Changes in the concentration of volatiles in extract obtained by SDE method

Compound	Days of storage			
	0	4	7	12
Phenylacetaldehyde	0.0132	0.0122	0.0296	0.0198
Hexadecanal	0.0710	0.0283	0.0269	0.0501
Octadecanal	0.0309	0.0169	0.0143	0.0163
Palmitic acid	0.0317	0.0302	0.0455	0.0706
Heptadecanoic acid	0.0155	0.0326	0.0261	0.0153
Stearic acid	0.0218	0.0210	0.0312	0.0430

Values shown in Table – mg substances/100 g yolk
See Fig. 3

method is relatively rapid, sensitive enough and gives reproducible results. The other two methods (SPEM and SDE) were rejected, due to lower sensitivity and reproducibility. SDE method also due to the different temperature condition (boiling of sample, which can lead to the formation of new compounds primarily not present in fresh eggs) during extraction of volatiles.

CONCLUSION

Three methods for the isolation and determination of egg volatiles, namely dynamic headspace (Purge and Trap), static headspace (Solid Phase of Microextraction – SPME) and extraction according to Likens-Nickerson by simultaneous distillation-extraction (SDE) with diethyl ether as organic solvent, were experimentally validated. The extracts were analyzed by GC/FID. The volatiles in an extract obtained by SDE method were identified by GC/MS. The volatiles in an extract obtained by SPME and Purge and Trap method have not been identified until now. The changes in volatiles during storage of eggs using the above mentioned methods were studied.

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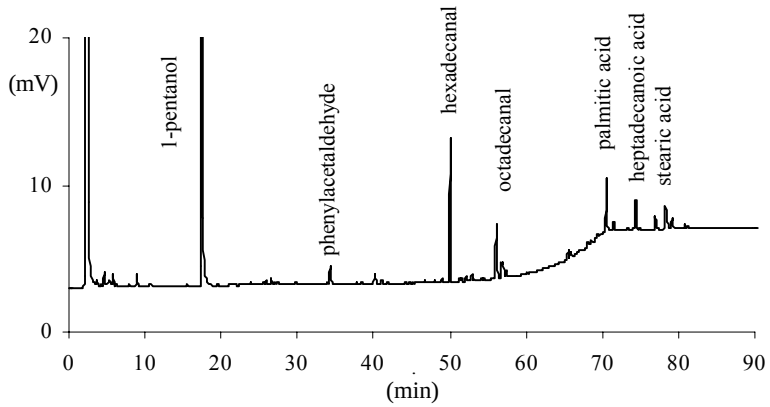

Fig. 3. Chromatogram of volatiles in extract obtained by SDE method

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Received for publication January 14, 2002
Accepted for publication January 28, 2002

Souhrn

ADAMIEC J., DOLEŽAL M., MÍKOVÁ K., DAVÍDEK J. (2002): **Změny koncentrace těkavých látek ve vejcích během skladování**. Czech J. Food Sci., **20**: 79–82.

Kvalita vajec je úzce spojena s jejich čerstvostí. Byly studovány nové možnosti stanovení čerstvosti, založené na změně koncentrace těkavých látek ve vejcích během skladování. Byly porovnávány tři extrakční metody: dynamický headspace (Purge and Trap), statický headspace (Solid Phase of Microextraction – SPME) a extrakce podle Likense-Nickersona (simultánní destilační extrakce – SDE) s organickým rozpouštědlem diethyletherem. Extrakty byly analyzovány GC/FID. Těkavé látky získané metodou SDE byly identifikovány GC-MS. Jde především o aldehydy, alkoholy, kyseliny a estery. Těkavé látky získané metodami SPME a Purge and Trap nebyly dosud identifikovány. Změny těkavých látek během skladování byly sledovány užitím uvedených metod.

Klíčová slova: kvalita vajec; změny během skladování; těkavé látky; Purge and Trap; Solid Phase of Microextraction, simultánní destilační extrakce

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