

Optimisation of a Headspace Solid Phase Microextraction (HS-SPME) Method to Determine Hexanal in Baby Foods

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Abstract: Fat oxidation during storage of baby foods gives rise to primary and secondary oxidation products. Among the latter, aldehydes are particularly important from a toxicological point of view and in relation to the organoleptic alteration. In baby foods one of the main volatile compounds is hexanal, resulting from the oxidation of linoleic acid. Hexanal content can be used as an indicator of lipid oxidation in these products.

Objective: To set up and validate a HS-SPME-GC method useful to measure the hexanal content in baby foods.

MATERIALS AND METHODS

Samples. Baby foods based on milk and cereals were used.

SPME fibre. Hexanal was extracted using a SPME device with a 85 µm CarboxenTM on polydimethylsiloxane (CAR/PDMS) StableFlexTM fibre (Supelco).

GC. An Equity 5 capillary column (Supelco; 30 m × 0.53 mm ID × film thickness 5 µm) installed on an Autosystem XL Perkin Elmer GC equipped with a flame ionisation detector (FID) and a split/splitless manual injector were used.

Procedure. 4 ml (c.a. 3.8 g) of baby food were sealed in a 10 ml vial with a PTFE/silicone septum. The following analytical conditions were applied:

Preheating	15 min (with stirring)/37°C
SPME sampling	45 min (with stirring)/37°C
GC oven	40°C, 5 min → 100°C (4°C/min) → 220°C, 10 min (17°C/min)
Carrier gas	H ₂ at 23.3 cm/s
GC injector	250°C (splitless)
GC FID	300°C

RESULTS

Under optimal conditions hexanal detection and quantification limits were 0.99 and 3.30 ng/g, respectively. The precision showed a relative standard deviation ranging from 0.86 to 3.11%, depending on the analysed baby food. A good linearity was obtained in the range from 2.6 to 107.7 ng/g added to the sample ($y = 0.023x + 0.231$; $r = 0.998$).

Acknowledgements: To Hero España S.A. for providing the samples and financial support for this study.

As Compared to Bovine Serum Albumin, Sodium Caseinate Either Reduces or Increases the Oxidative Stability of Oil-in-Water Emulsions According to the Location and Availability of Iron

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Abstract: Many foods can be described as protein-stabilized emulsions in which the lipid phase tends to oxidize, causing losses in the sensory and nutritional qualities. Lipid oxidation in emulsions is mainly controlled by the properties of the interface. Thus, controlling both protein composition and protein interactions with the prooxidant and antioxidant compounds, could be a tool for improving shelf life and overall quality of the products [1]. The aim of this study was to compare the oxidative stabilities of sunflower oil-in-water emulsions stabilized by either bovine serum albumin (BSA) or sodium caseinate (NaCas). Emulsions containing 30 vol.% stripped sunflower oil and 70 vol.% protein solution (20 g/l; pH = 6.5), with similar oil droplet size distributions were stored at 50°C in the dark in rotated closed vials. As shown by measurement of oxygen uptake in the headspace of the emulsions, in the presence of the water soluble chelating agent EDTA (100 µM), the NaCas-stabilized emulsions oxidized slower than the BSA-stabilized ones. In these conditions, the metal ions present in the emulsions remained in the aqueous phase of the emulsions and could not catalyze lipid oxidation. Thus the higher antiradical activity of NaCas as compared to BSA, demonstrated by ESR measurement of free radicals in the emulsions in presence of the spin probe N-ter-butyl- α -phenylnitron (PBN), became prominent. It protected the lipid phase against oxidation. In the presence of low EDTA concentration (µM), probably very close to the total concentration of metal ions in the emulsions, NaCas sometimes oxidized faster, sometimes more slowly than BSA emulsions. When EDTA was not present, NaCas-emulsions oxidized faster than the BSA-emulsions. In this condition, NaCas attracted the metal cations at the oil-water interface, due to the chelating properties of the proteins and the higher negative charge of the oil droplets than in presence of BSA. Metal ions were therefore strategically located to catalyze lipid oxidation. Other factors such as interfacial film thickness might also contribute to differences of oxidation between the two types of emulsions.

Acknowledgements : The region Pays de la Loire and INRA (France) for financial help (VANAM program) and the support of the European Community for the access to Levnedsmiddelcentret Major Research Infrastructure (LMC-MRI) (improving Human Potential Program).

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Fluorescence of Oxidizing Oil-in-Water Emulsions

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Abstract: Front-face fluorescence spectroscopy was used to characterize modifications of fluorescence spectra of oil-in-water emulsions, stabilized by bovine serum albumin (BSA) or sodium caseinate during aging at 50°C. Commercial sunflower oil or the same oil stripped of tocopherols, were used as the apolar phase of the emulsions. The 3D-fluorescence spectra of the emulsions were characterized by three groups of fluorescent pigments: (i) protein aromatic amino acid residues, mainly tryptophanyl residues (Trp); (ii) pigments initially present in the oils: tocopherol and others; (iii) new fluorescent pigments due to reactions of lipid oxidation products with the proteins. During oxidation of the emulsions, the fluorescence intensities of protein Trp and oil's pigments decreased whereas the new fluorescent pigments were produced. As expected, and in agreement with development of lipid oxidation, the changes were slower for the unstripped than for the stripped oil. The relative fluorescence intensity of protein Trp decreased slightly faster in the caseinate-stabilized emulsions than in the BSA ones. Increases in fluorescence intensity of new pigments showed no difference.

Acknowledgements: The region Pays de la Loire and INRA (France) for financial support (VANAM program).

Structural and Chemical Modifications of β -Lactoglobulin Induced by Aldehydes

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Abstract: Aldehydes are odour-active compounds issued from reactions such as lipid oxidation. They react with other food constituents such as proteins [1, 2], that decreases their availability as aroma compounds, but also induces alterations of the proteins. This study was aimed to evidence the structural and chemical modifications of β -lactoglobulin in the presence of aldehydes varying in their unsaturation. β -Lactoglobulin solutions (1 g/l; 20mM phosphate buffer, pH 6.8; 80mM NaCl) were stored at 40°C in the presence of hexanal, 2-hexenal or 2,4-hexadienal (aldehyde/protein molar ratio = 25) for 3 days. Whatever the aldehyde, formation of more hydrophobic, modified protein was evidenced by reverse phase HPLC. The fixation of the aldehydes by the protein was evaluated by headspace-gas chromatography. UV-Vis, circular dichroism and fluorescence spectra evidenced, only in the presence of the unsaturated aldehydes, changes in the protein structure, in the environment of its tryptophanyl residues and formation of new fluorescent compounds. Covalent protein dimmers, not due to disulfure bonds, were also produced. Analysis of amino acid composition and mass spectrometry of tryptic hydrolysate of the reaction mixtures gave information on the nature of the chemical modifications.

Acknowledgements: The region Pays de la Loire, INRA (France) for financial support (VANAM program).

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