

## Background

Optical brighteners (OB) are substances used in paper and board to whiten the paper. Typical substances for this application are derivatives of the 4,4'-diaminostilbene-2,2'-disulfonic acid. According to BfR recommendation XXXVI they can be used for paper and board food contact materials up to 0.3% but should not be detectable in a visual test system with food simulants as described in DIN EN 648 [1; 2]. Cardboard boxes made of recycled paper are used as food packaging materials for dry food, but also kitchen tissues can be produced using recycled fiber material. The recycling process does not remove these substances from the fibers and for this reason they might migrate into food.

## Summary

A chromatographic method using HILIC-HPLC-FLD for quantifying OBs was established. In the raw material for the recycling process OB could be determined between <0.1 mg OB equivalent/kg and 2100 mg OB equivalent/kg paper. In food packagings of recycled board the sum was determined between < 0.1 mg OB equivalent/kg (fresh fiber board) and 620 mg OB equivalent/kg board. A migration of optical brighteners into food (egg white) was observed in amounts of max. 5.3 µg/sdm (LOD <0.2 µg/sdm, 1.7 µg/sdm correspond to 10 ppb in the food but only 4.2 µg/sdm (25 ppb) correspond to the visual detection limit of the method set out in DIN EN 648).

## Material and Methods

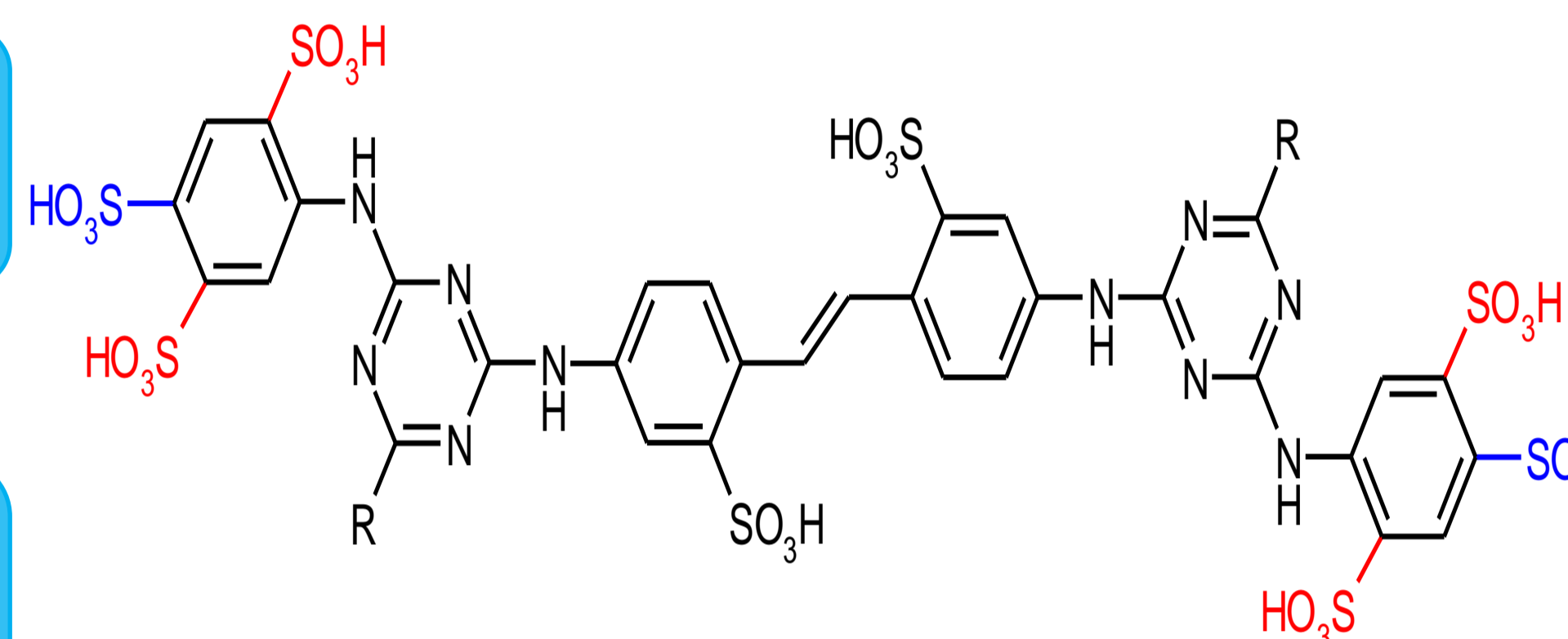
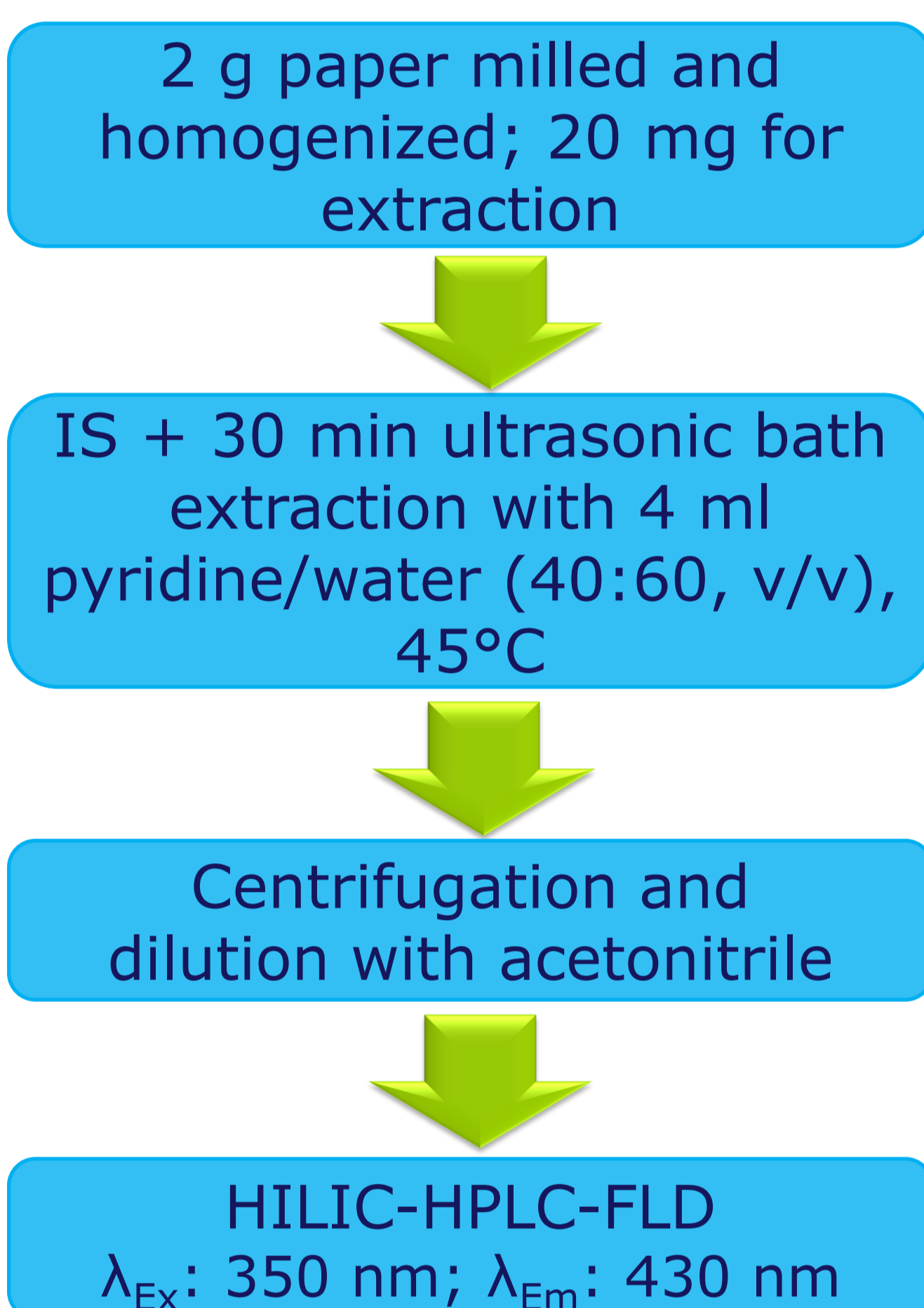
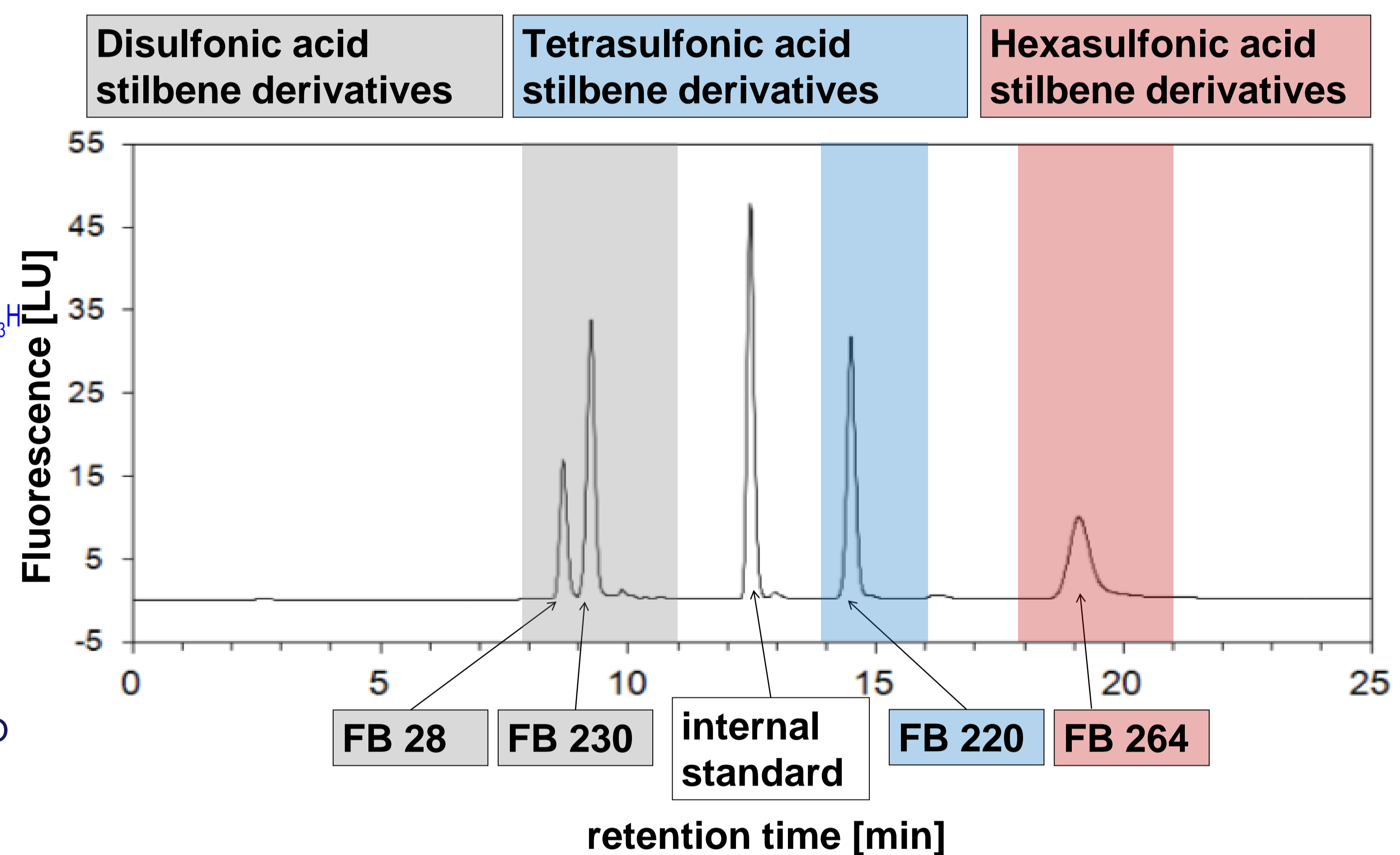


Fig. 1: structure of disulfonic acid stilbene derivate (black -SO<sub>3</sub>H), of tetrasulfonic acid stilbene derivate (black + blue -SO<sub>3</sub>H) and of hexasulfonic acid stilbene (black + blue + red -SO<sub>3</sub>H)

Fig. 2: Chromatogram of the stilbene derivatives analysed by HILIC-HPLC-FLD  
λ<sub>Ex</sub>: 350 nm; λ<sub>Em</sub>: 430 nm  
Eluent: Acetonitrile, 5mM ammonium acetate buffer (pH 6,7)



## Results

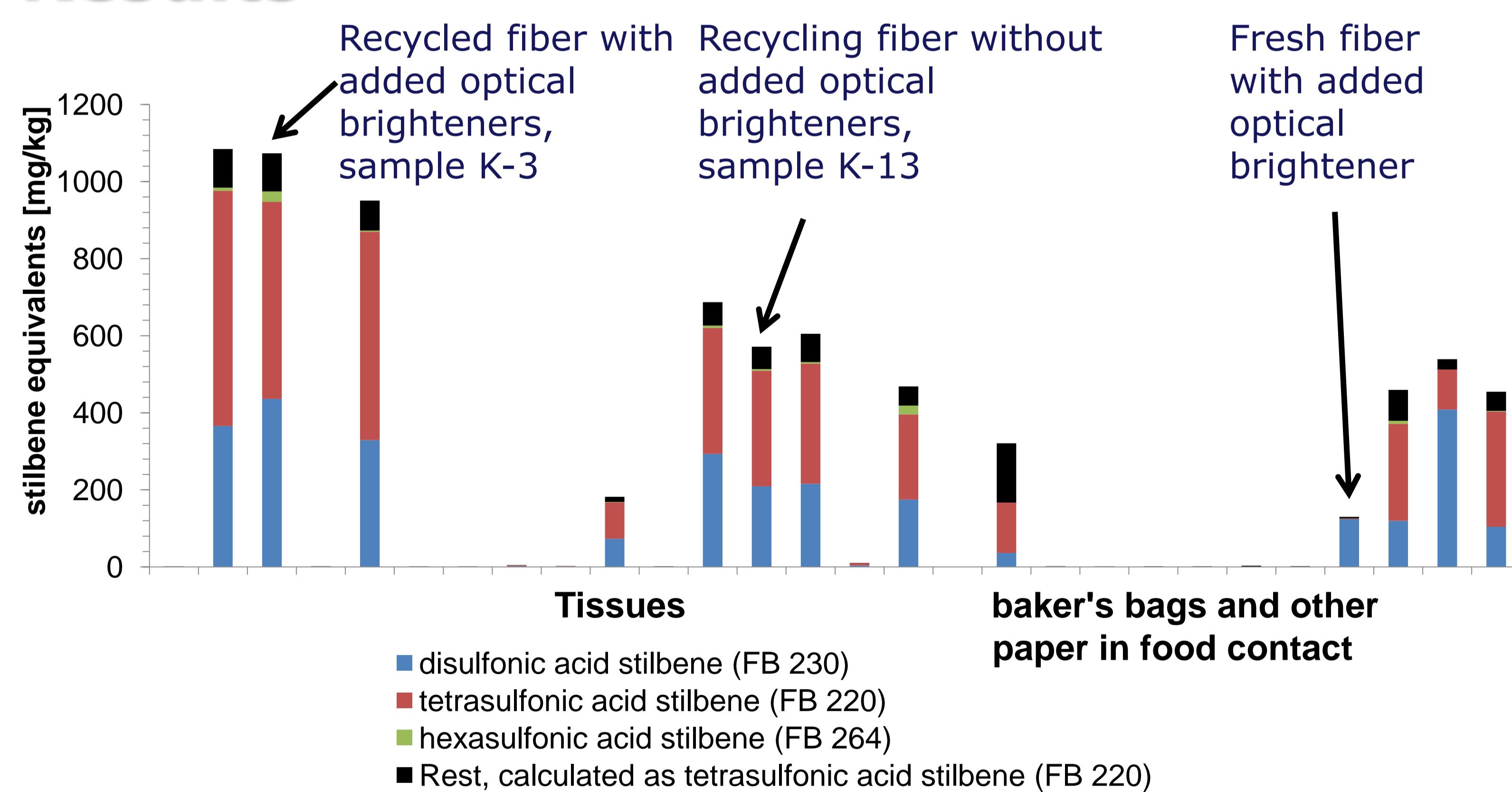


Fig. 3: Content of di- tetra- and hexasulfonic acid stilbene derivatives in kitchen tissues and other papers in food contact

### Analysing kitchen tissues and paper in contact with food:

- some kitchen tissues from recycled fiber have been produced under addition of optical brighteners (total OB amount between 900 and 1100 mg/kg), e.g. sample K-3
- for recycling tissues without OB addition OB amounts ranged between 200 and 750 mg/kg
- only one type of OBs is added to fresh fiber (either di- or tetrasulfonic acid stilbene) (fig.3)
- most fresh fiber samples were not optically brightened

### Acknowledgment and Literature

This project was financed by the Federal Ministry of Food, Agriculture and Consumer Protection (BMELV), Germany, managed by the Federal Office for Agriculture and Food (BLE), Germany.

[1]: The Federal Institute of Risk Assessment (BfR), Recommendation XXXVI, 2012  
[2]: DIN EN 648:2006, Paper and board intended to come into contact with foodstuffs - Determination of the fastness of fluorescent whitened paper and board, 2006

### Migration testings with food:

- migration of OBs from kitchen tissues K-3 and K-13 on eggs is shown by visual detection under a UV light (266nm) (fig. 4)
- Contents up to 5.3 µg/sdm could be detected by HILIC-HPLC-FLD

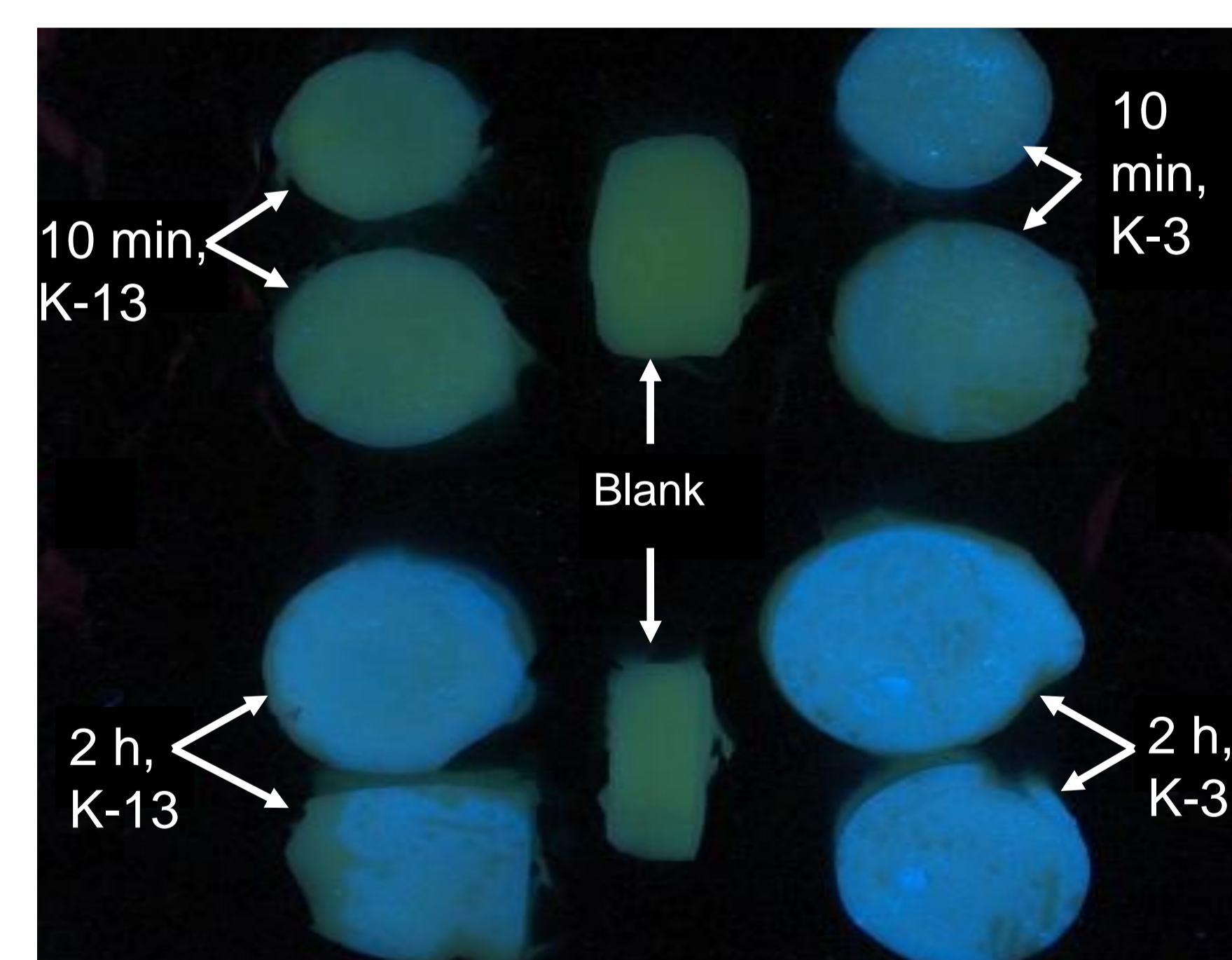


Fig. 4: Eggs in contact with wet kitchen towels for 10 min and 2 h

K-3: tissue, recycled fiber optically brightened

K-13: tissue, recycled fiber

### Migration testings according to DIN EN 648:

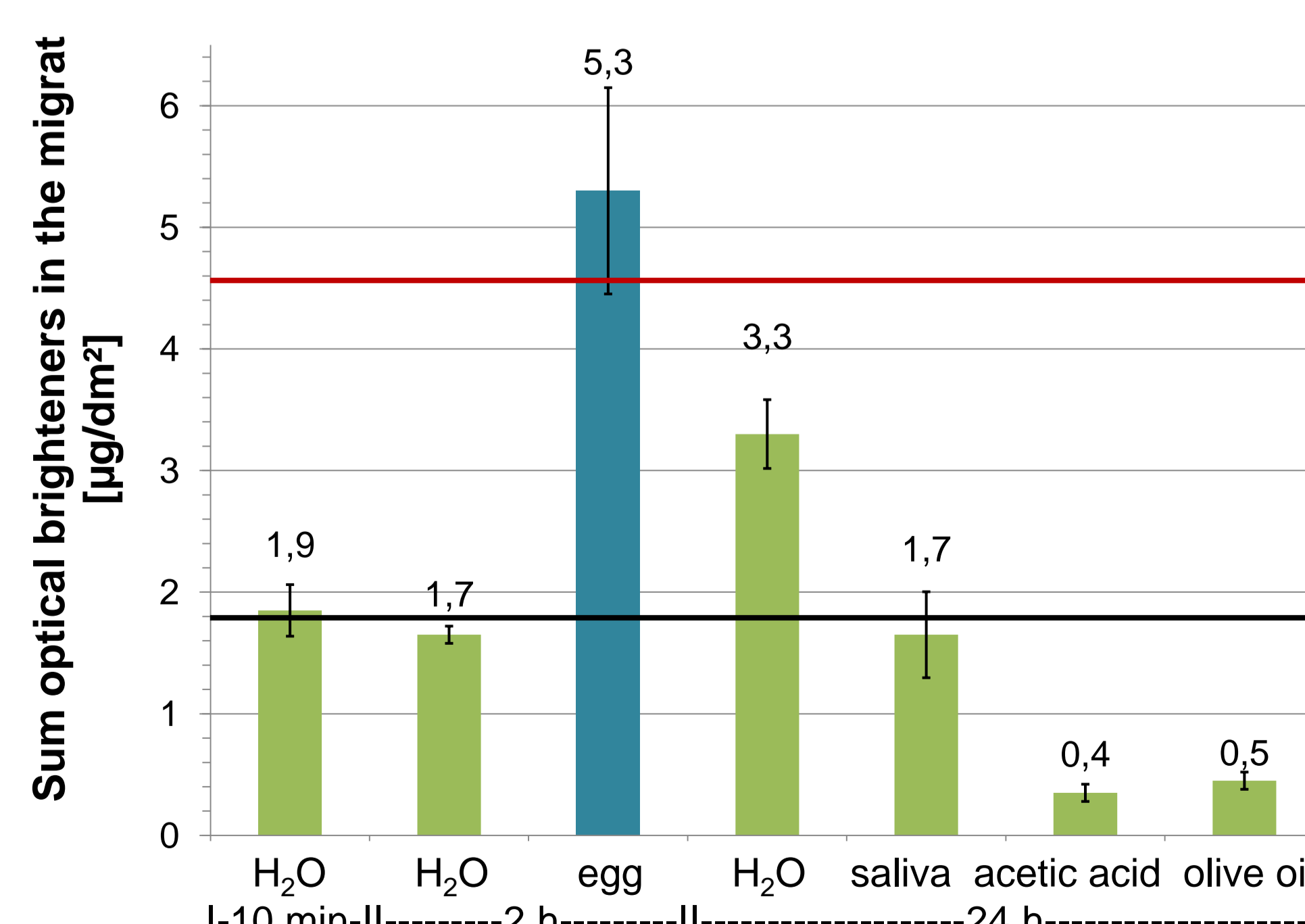


Fig. 5: Results of migration testings of sample K-3 analysed by HILIC-HPLC-FLD, test simulants according to DIN EN 648: water, saliva, acetic acid and olive oil  
red: amount of valuation level 4 of the DIN EN 648, black: 10 ppb limit

While migration tests for K-3 into simulants according to DIN EN 648 (fig.5) revealed an OB transfer below the visual limit (level 4), migration into egg-white was higher under the same conditions (fig.5, fig.4) even exceeding the visual limit (analytically proven).