



Influencing Absorption and Desorption of Ions in Human Hair

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Changing the Absorption and Desorption Properties of Human Hair by Ion-Induced Matrix Modification

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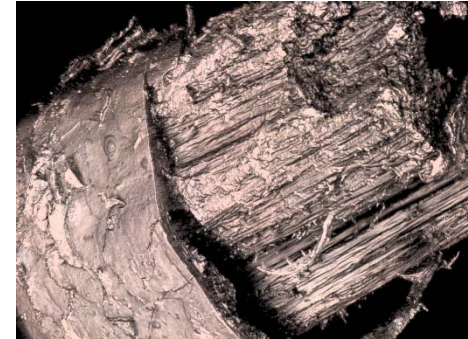
Franz Josef Wortmann (University Manchester)



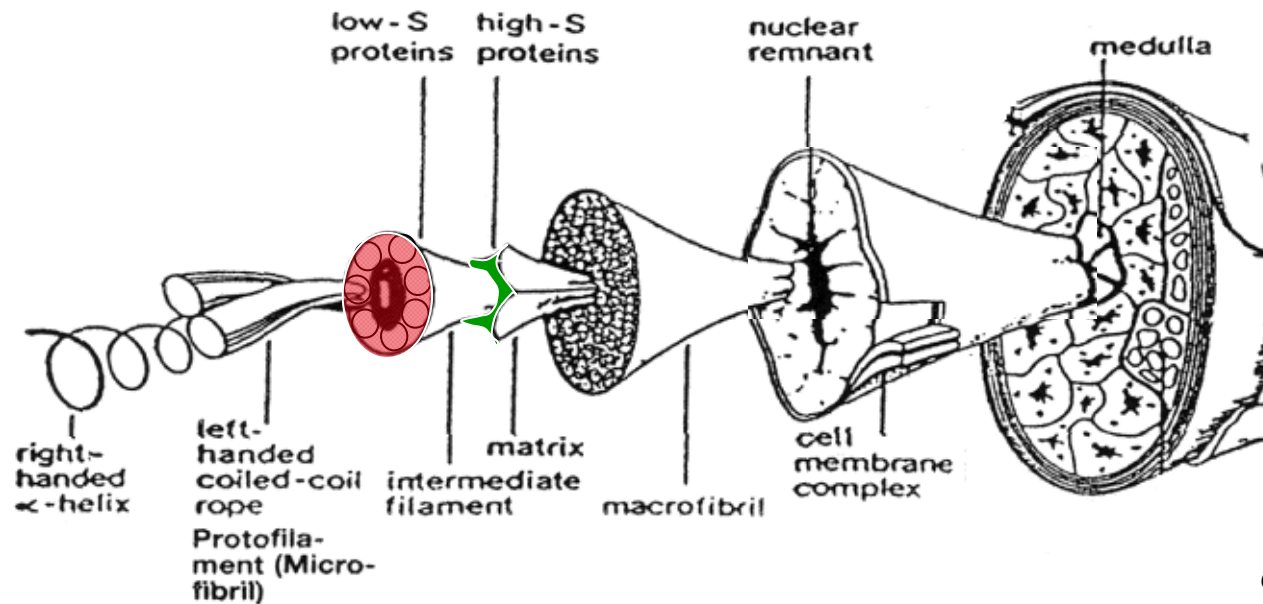
Excellence is our Passion

Content

- Keratin composition of hair
- Chemical oxidation of hair
- Effects of pH adjustments on the hair matrix
- Modification of absorption and desorption properties of hair
- Conclusions



Morphological Structure of Human Hair



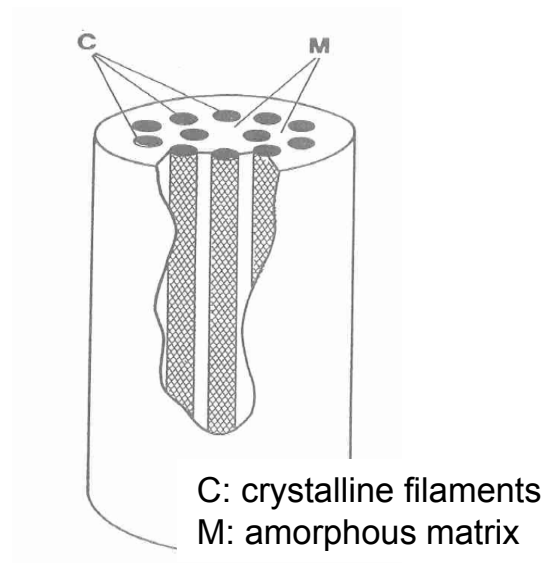
- Semi-crystalline intermediate filaments (IFs) are embedded in an amorphous matrix

Morphological Structure of Human Hair

“Simplified Models”

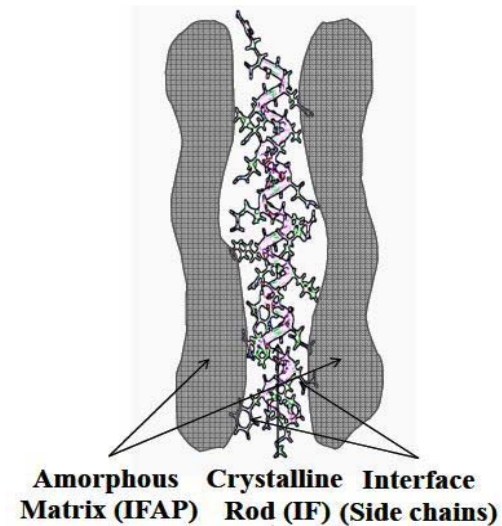
Two-phase model (2PM)

Feughelman 1959



"Three-phase" model (3PM)

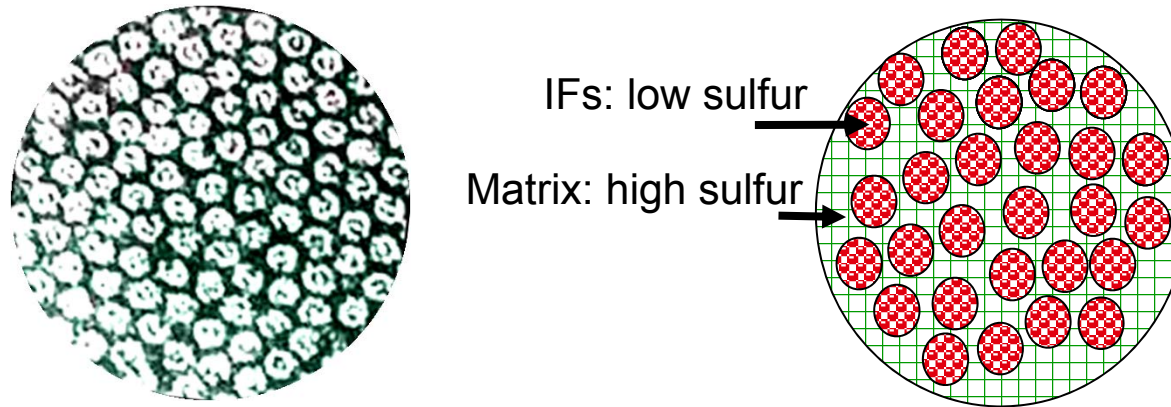
Popescu 2012



- 2PM: IFs and amorphous matrix are mainly responsible for the hair strength
- 3PM: The interface contributes significantly to the fiber stability

Composite structure of Human Hair

Fiber reinforced composite

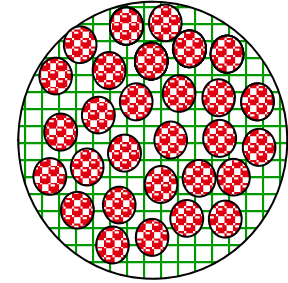


*SEM of transverse section of
sheeps wool: IFs (approx. 8 nm
diameter) by Parry 1997*

- Semi crystalline IFs are embedded in the amorphous protein matrix

Composite Structure of Human Hair

Matrix



- KAP – keratin associated proteins with high content of cystine
- Matrix stabilizes the embedded semi crystalline IFs
- Formation of cysteic acid due to chemical treatments
- Penetrable by water and the swelling component in hair
- Area for oxidative dye reactions

Bleaching Stress on Hair

Materials and formulation

- **Hair Samples:**

Kerling European Hair 7.0

- **“Ultra Bleaching”** (commercial product):

potassium persulphate mixed with a hydrogen peroxide solution (9%) in a ratio of 1:2, pH-value of 10.2-10.5 for 45 minutes



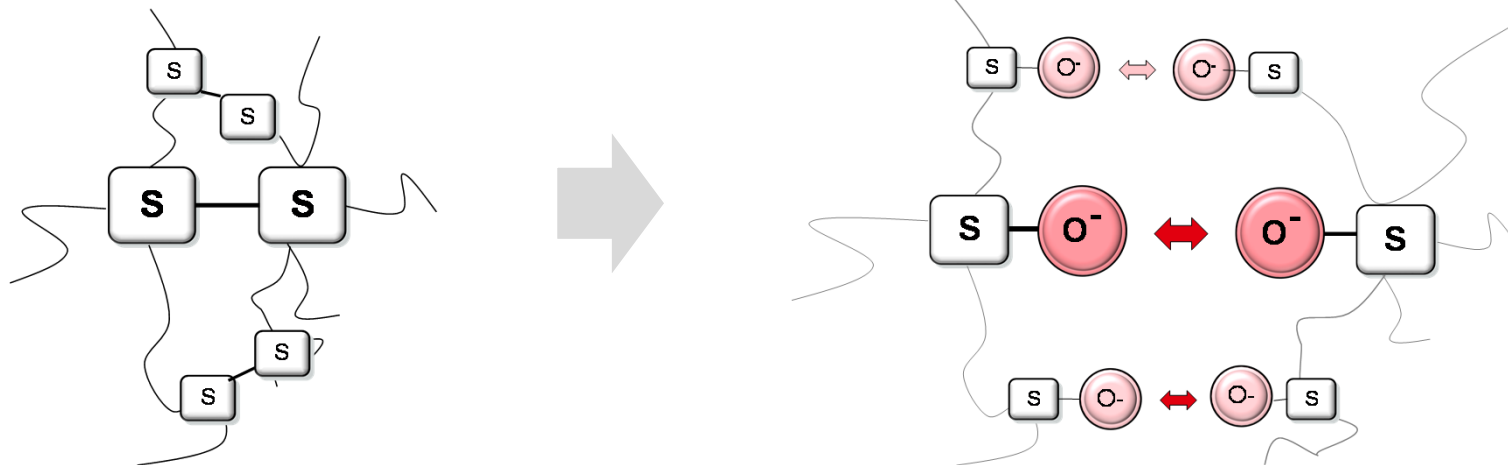
virgin/ untreated



ultra-bleached

Bleaching Stress on Hair

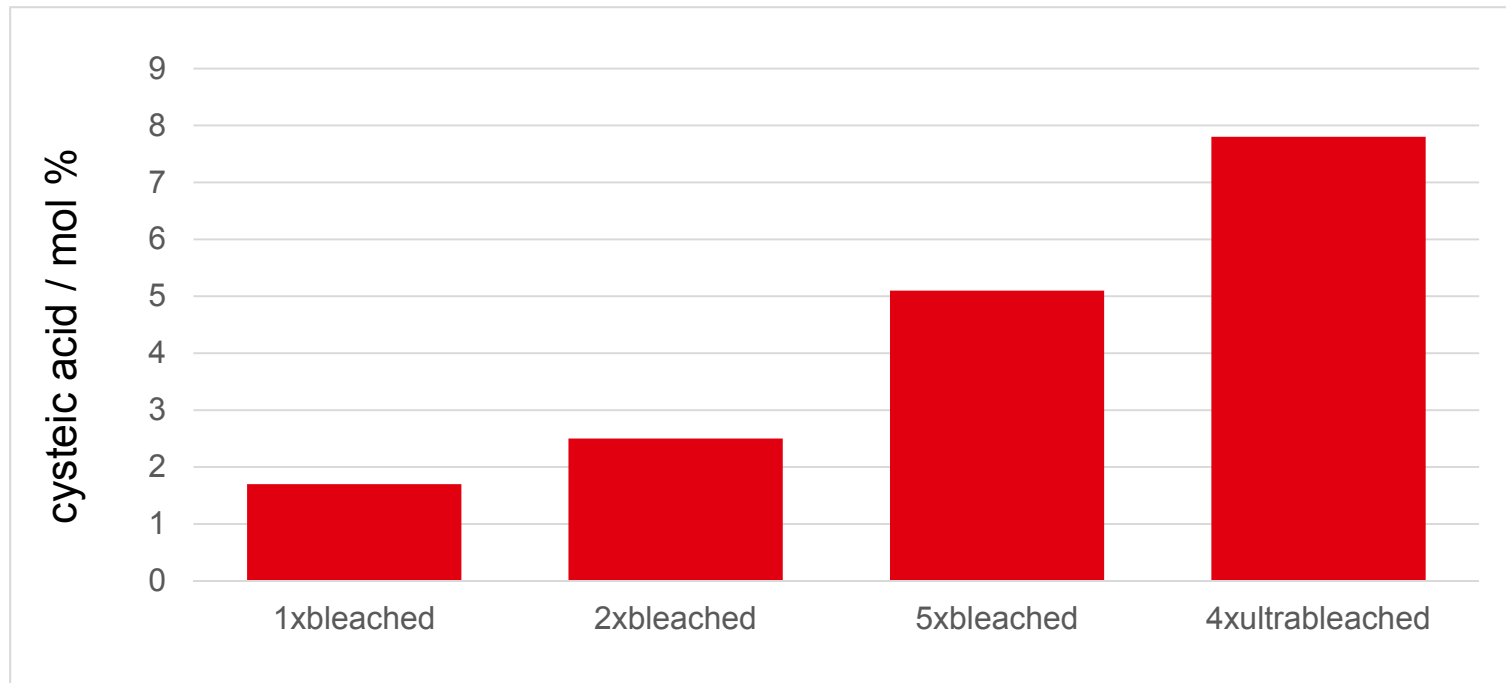
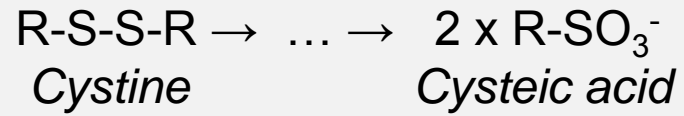
Cleavage of S-S bonds in the KAP-Matrix



- Bleaching leads to cleavage of cystine and the formation of cysteic acid (pKa1.3)

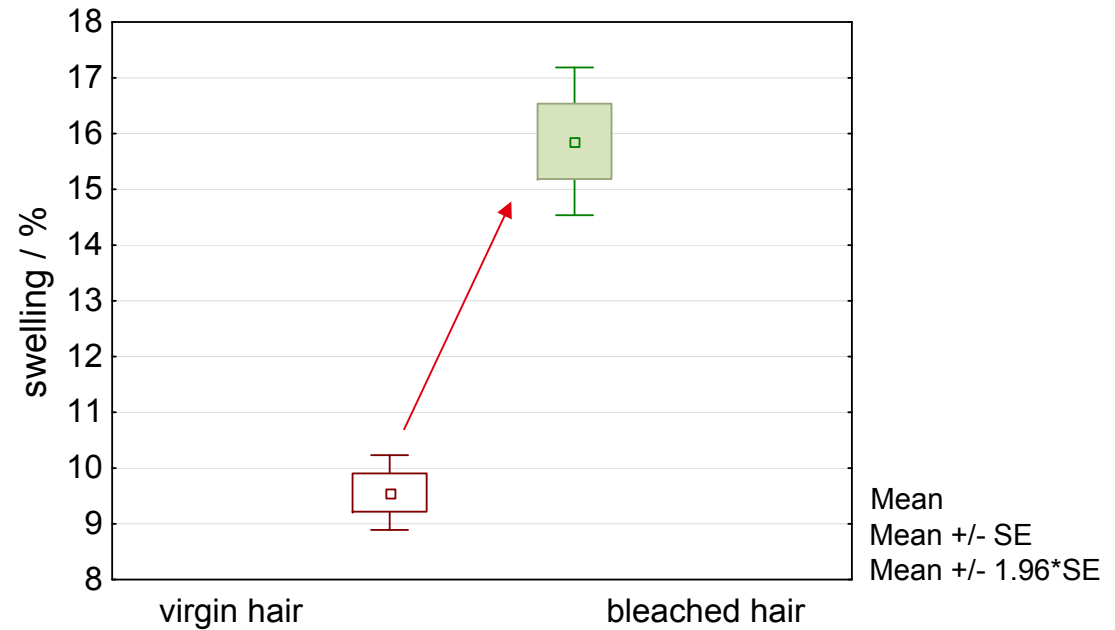
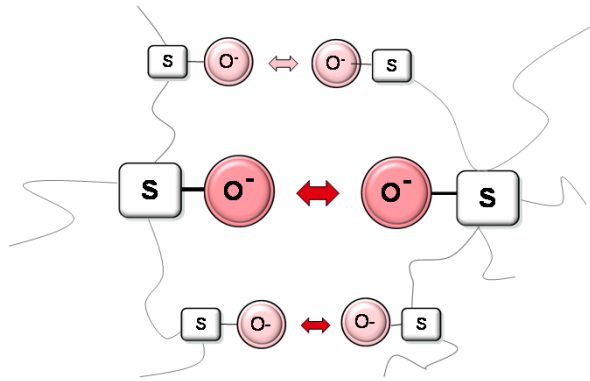
Bleaching Stress on Hair

Formation of cysteic acid



Bleaching Stress on Hair

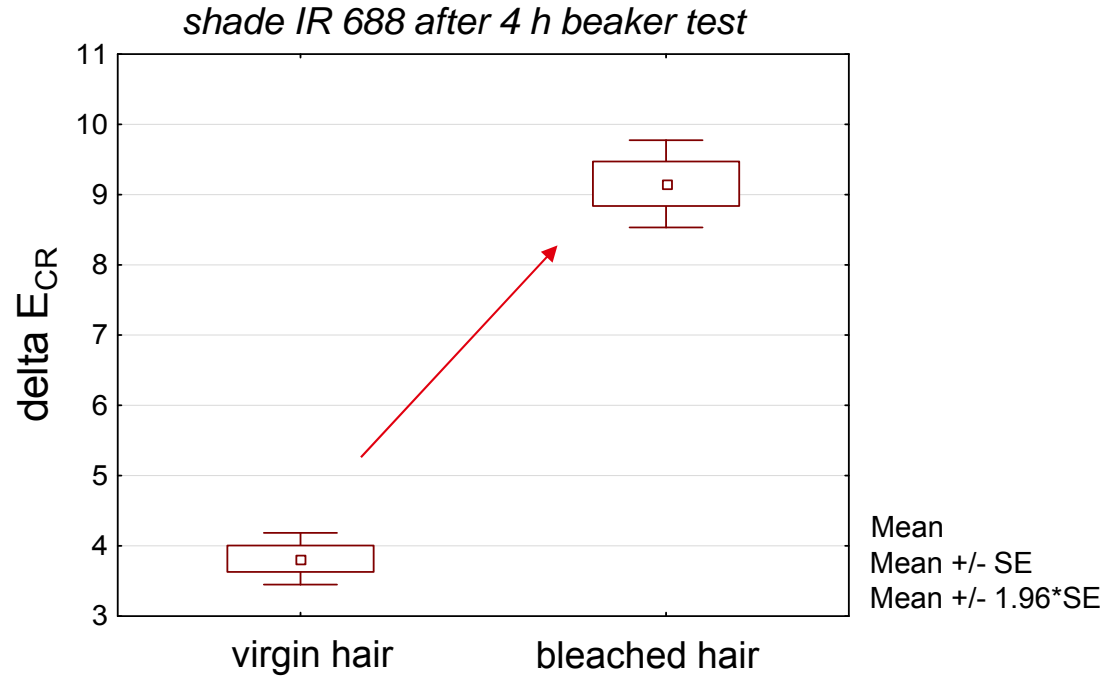
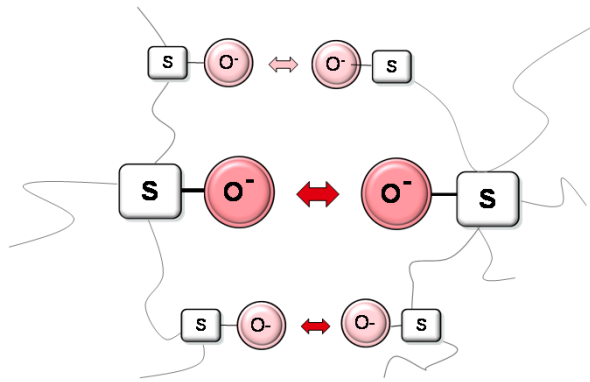
Effects on the swelling behavior



- Bleached hair swells approx. 50% more than virgin hair

Bleaching Stress on Hair

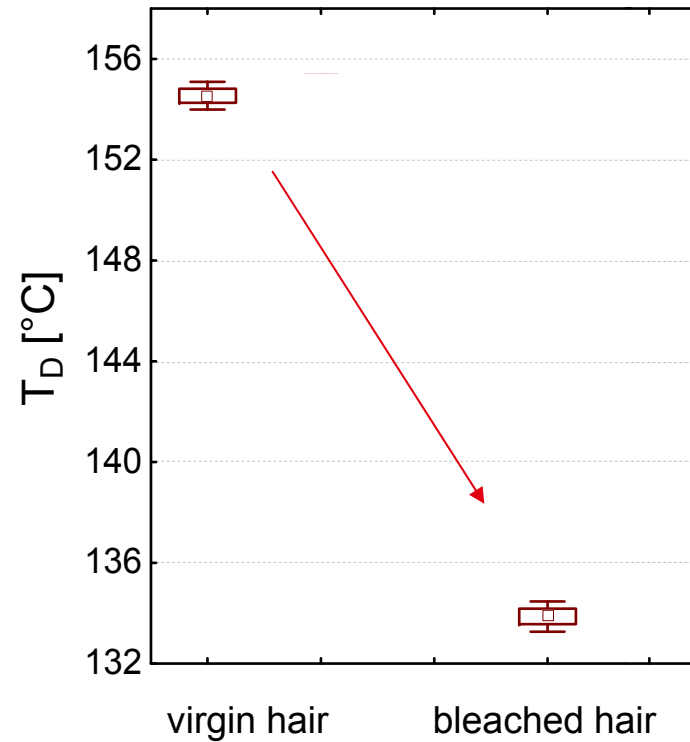
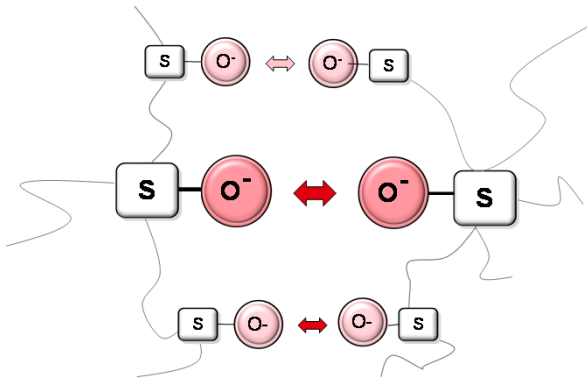
Effects on color retention



- Bleached hair losses approx. 50% more color than virgin hair

Bleaching Stress on Hair

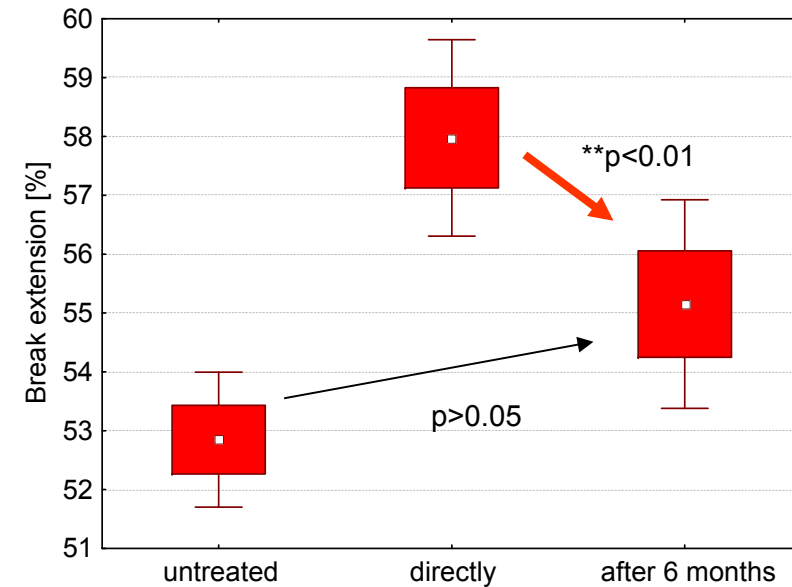
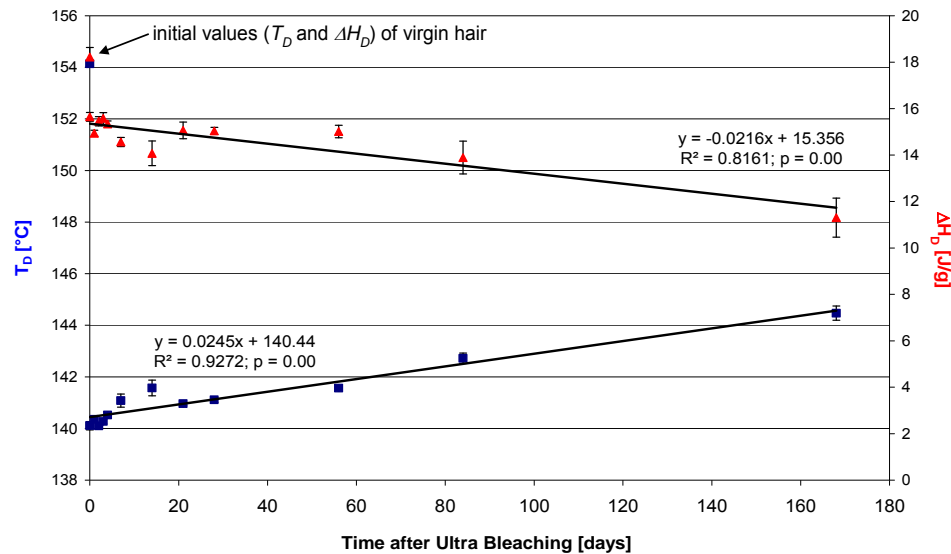
Effects on the thermal stability



- The denaturation temperature decreases strongly with bleaching

The “Self Recovery Phenomenon”

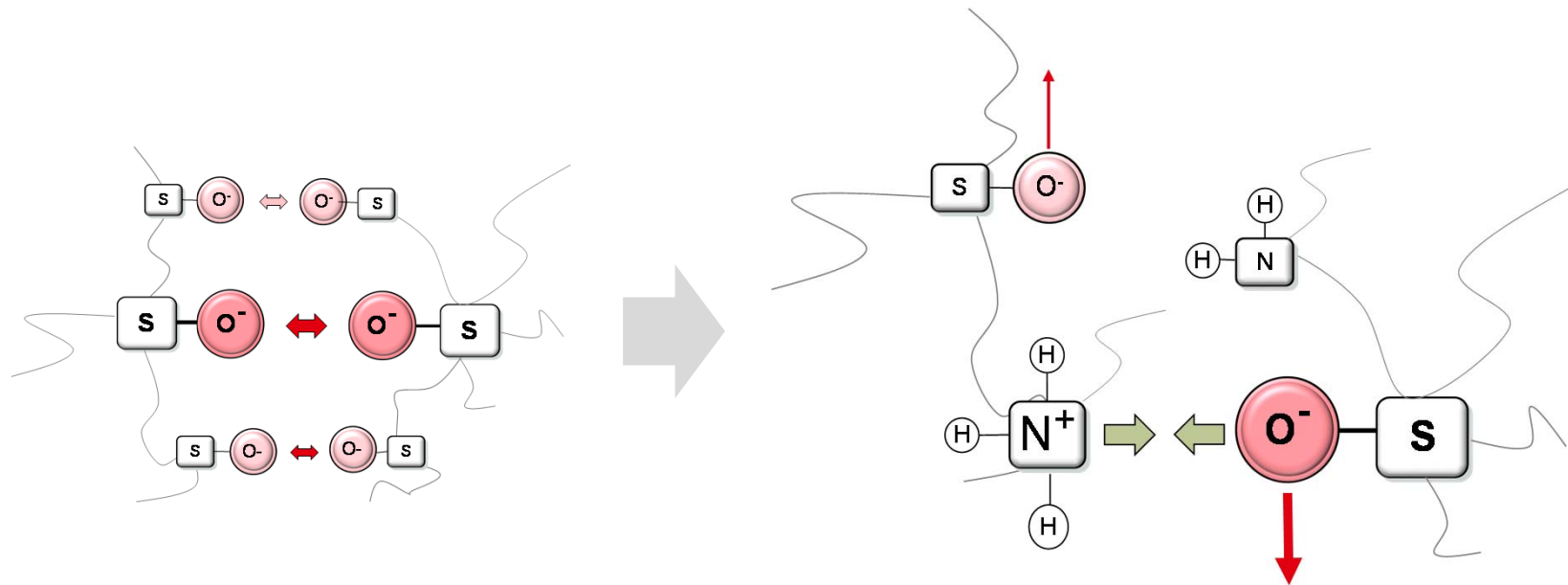
Tensile and DSC measurements on ultra bleached hair



- T_D increases and break extension decreases over a period of 6 months

Time-Related Inner Structural Changes

Hypothesis

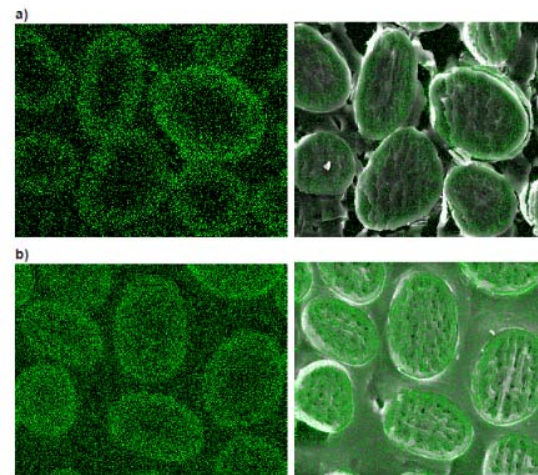
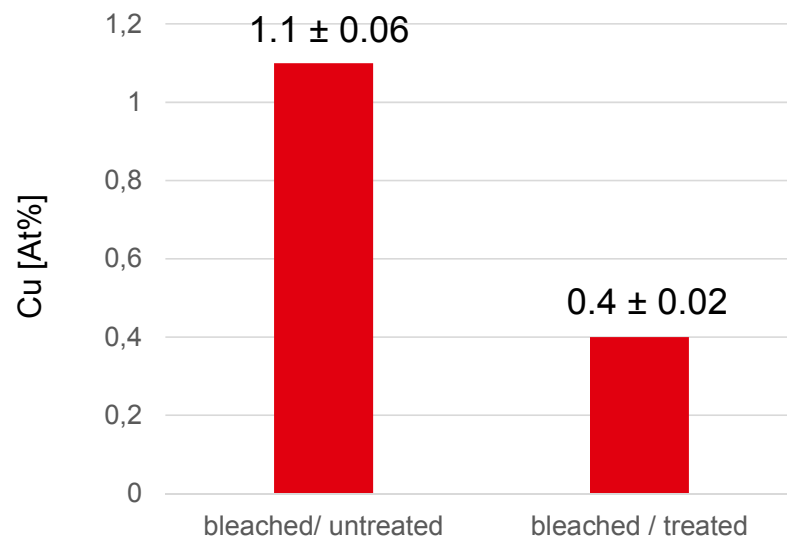


- Formed cysteic acid dives a reorganization process of the secondary protein structure within the amorphous matrix

Ionic-Modification of Matrix

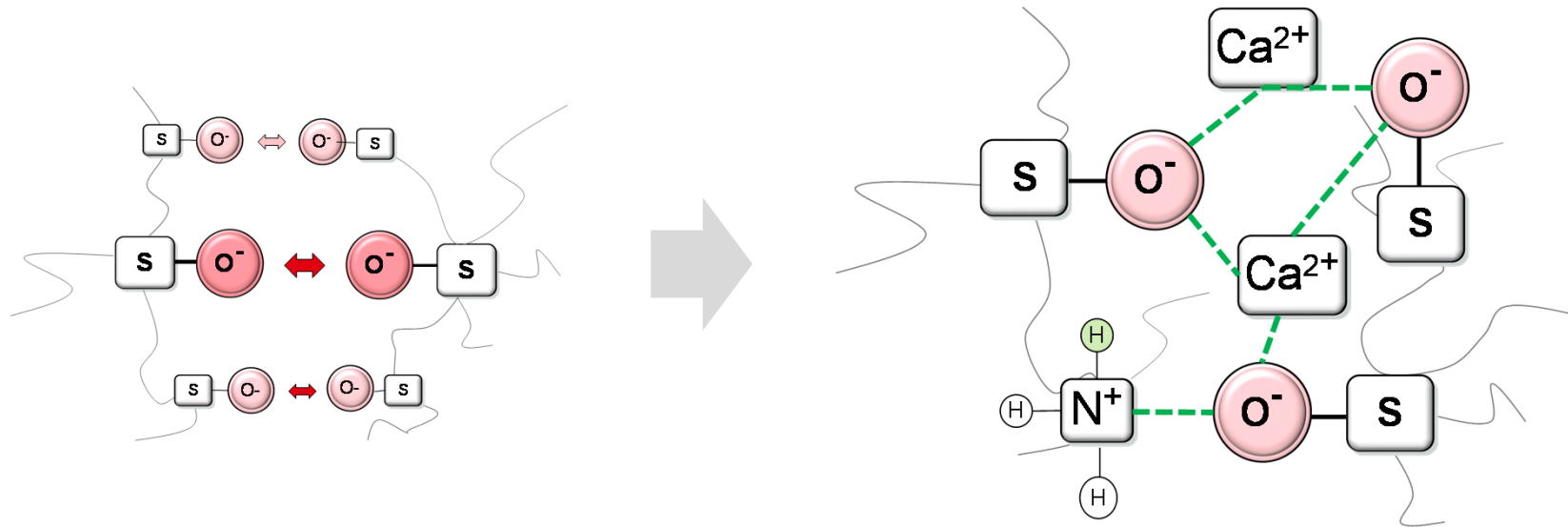
Influence on the uptake of Cu^{2+} ions

- EDX analysis of Cu atoms on 2 x bleached hair with and without pretreatment of 1 % EDTA before applying 1 % $\text{Cu}(\text{II})\text{SO}_4$



- EDTA and acetic acid pretreatments at pH 4.4 reduces the Cu uptake of hair up to 65 %

Ionic-Modification of Matrix Hypothesis



- Adjustment of an isoionic pH value and the presents of multivalent ions stabilizes the hair matrix by the formation of ionic bonds

Determination of Color Retention

Method

Hair Color: Schwarzkopf Igora Royal

Shades: 6-88 (dark red), 6-99 (violet), 9-98 (violet red)
7-77 (copper), 4-88 (dark red), 5-88 (dark red)
6-68 (red brown), 0-88 (light red)

Shampoo: 2% cocoyl amphoacetate, 4%
cocoamidopropyl betain, 8.8 % LES

Beaker Screening test:

20 % shampoo solution for 4 hours stirring

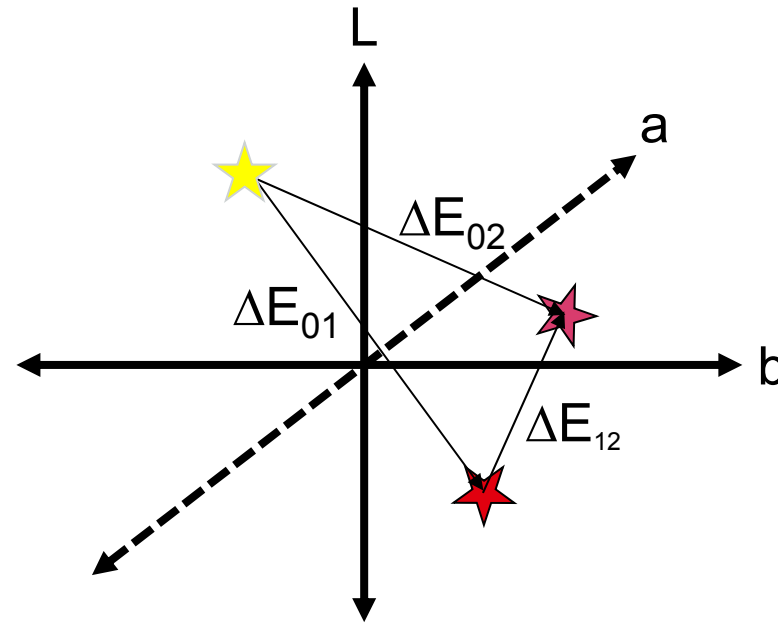
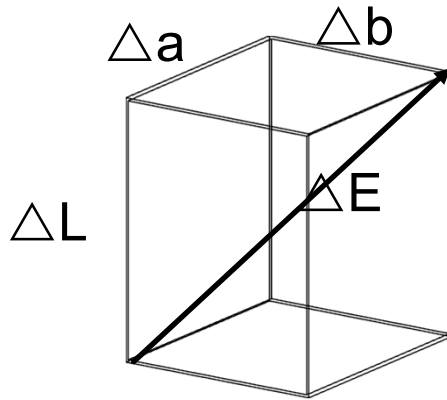
Ultra sonic washing simulation: 2,5 % shampoo
solution 5 min ultra sonic bath (3 hand washes)

Hand washes on strands: 0,05 g shampoo/g hair, 30
sec shampooing, 30 sec application, 1 min rinse off



Color Retention and Color Shift

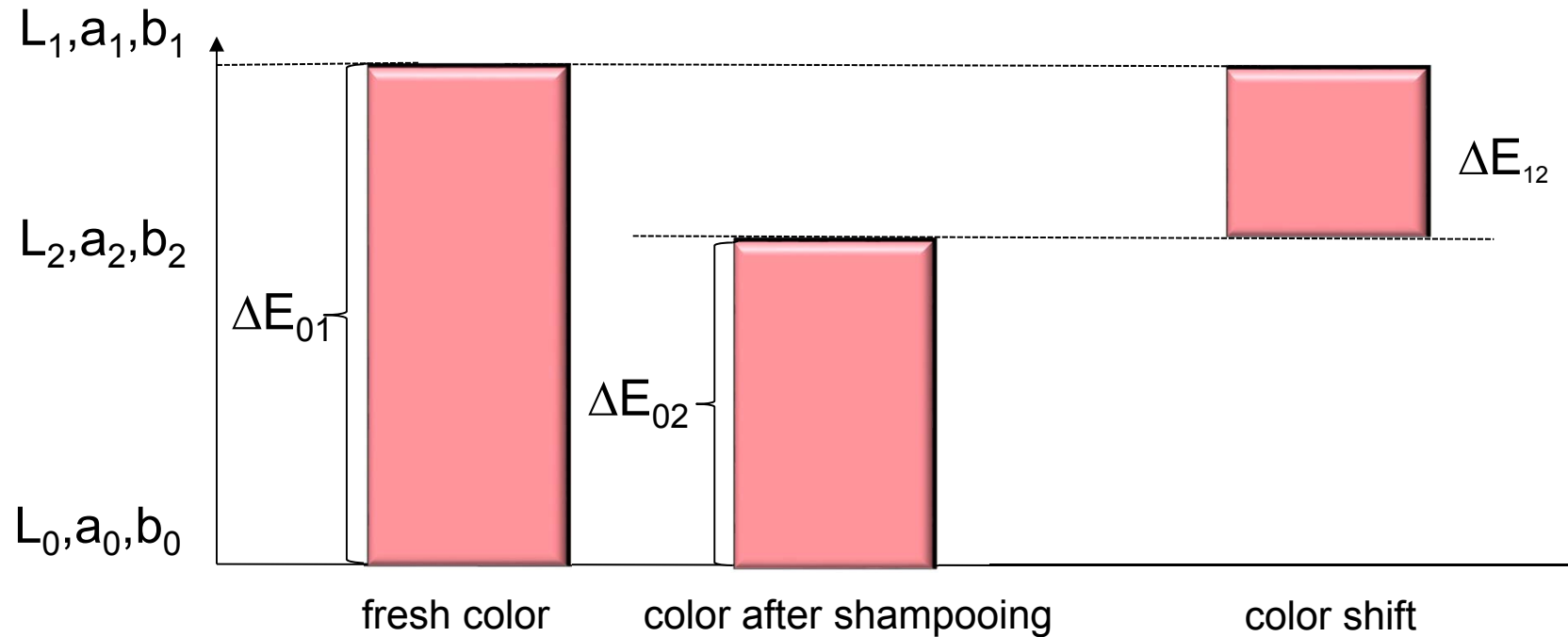
CIE-L-a-b Color Analysis



$$dE = \sqrt{\left((L_c - L_s)^2 + (a_c - a_s)^2 + (b_c - b_s)^2\right)}$$

Color Retention and Color Shift

CIE-L-a-b Color Analysis

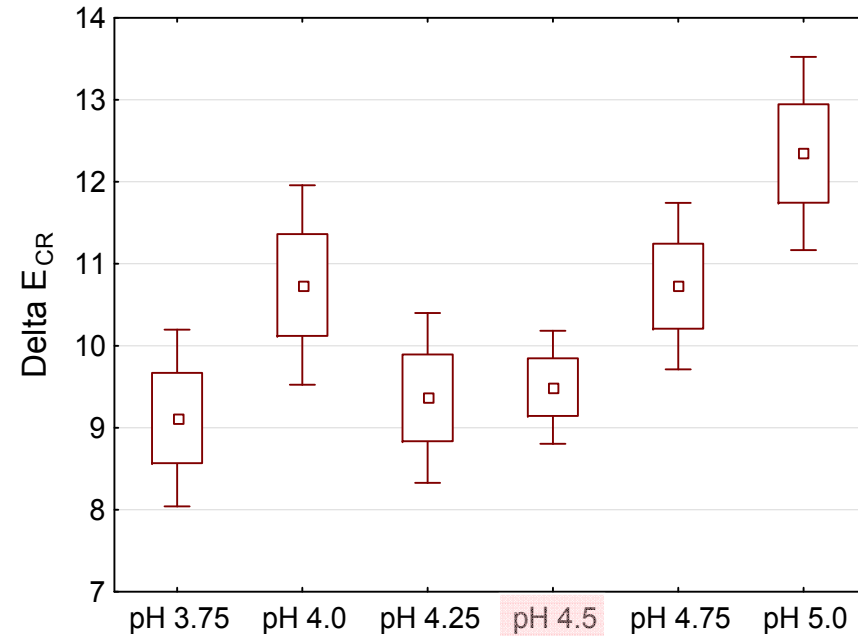
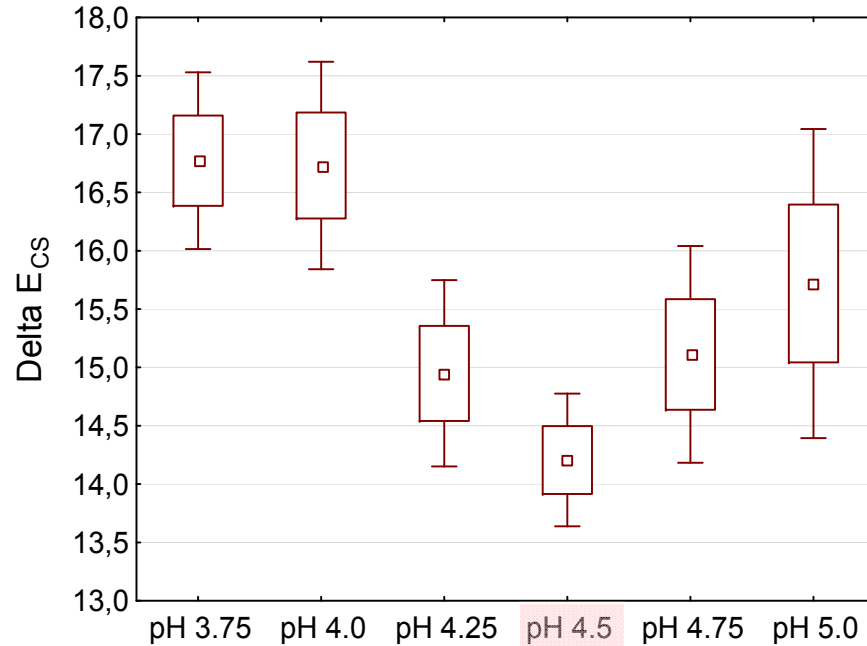


Color Retention: $\Delta E_{CR} = \Delta E_{01} - \Delta E_{02}$

Color Shift: ΔE_{CS}

Ionic-Modification of Matrix

Influence of pH on color shift ΔE_{CS} and color retention ΔE_{CR}

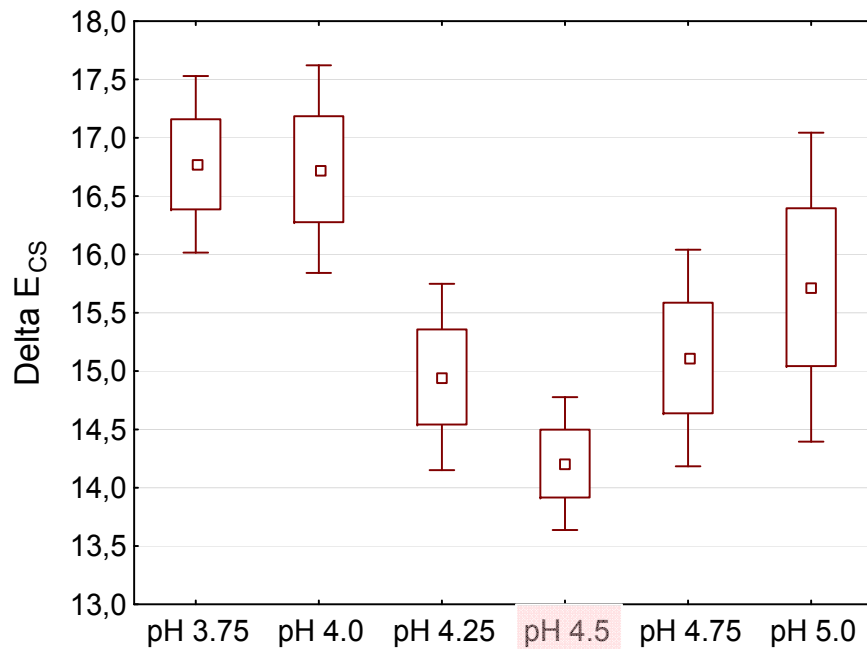


Mean
Mean +/- SE
Mean +/- 1.96*SE

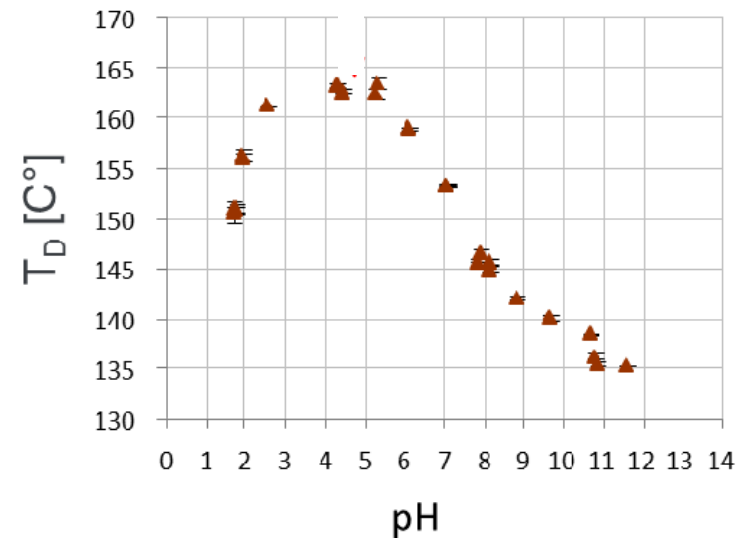
- Strong differences between ΔE_{CS} and ΔE_{CR}
- Highest color stability at pH 4.5 in the range of the isoionic point of hair

Ionic-Modification of Matrix

Influence of pH on color ΔE_{CS} and denaturation T_D



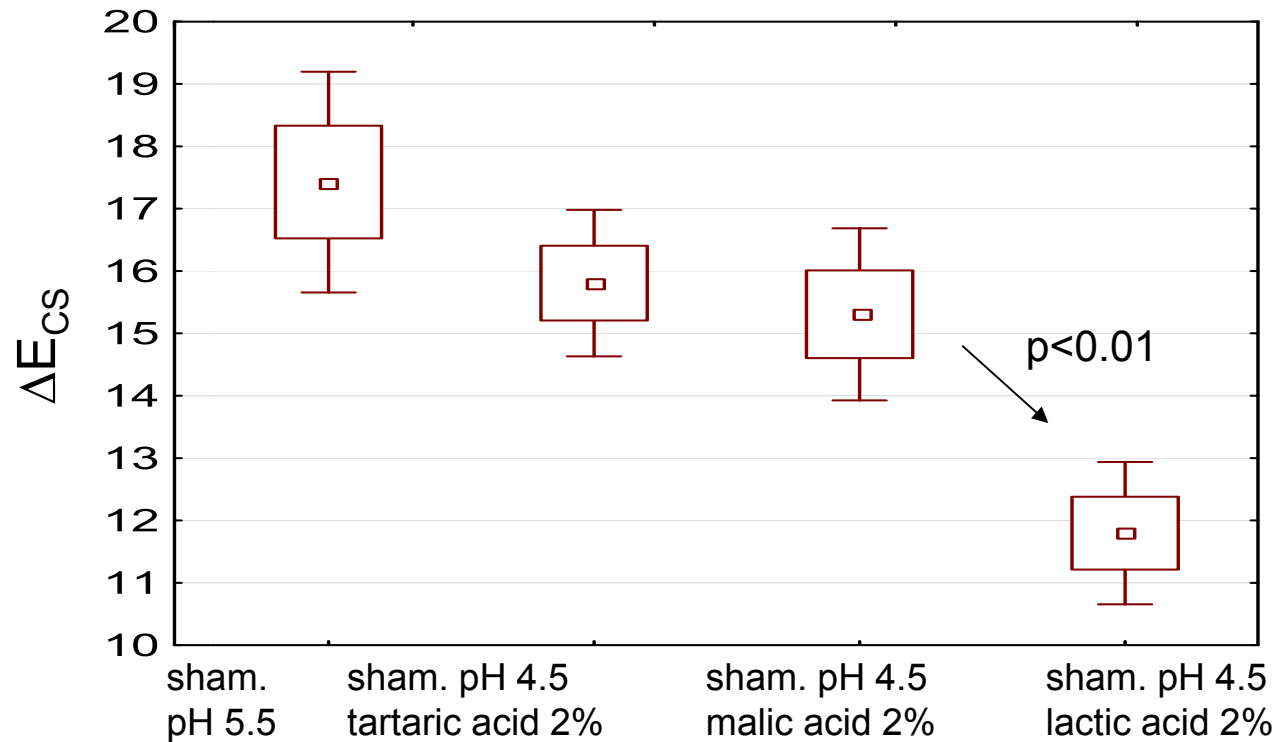
DSC measurement of 2 x bleached hair 24 h in pH controlled aqueous solution



- Thermal stability and color stability show maxima at pH 4.5

Ionic-Modification of Matrix

Influence of organic acids on the color shift ΔE_{CS}



- Significant differences between organic acids
- Ca lactate shampoo shows the strongest effect

Ionic-Modification of Matrix

Influence of organic acids on the color shift ΔE_{CS}



sham.pH 5.5

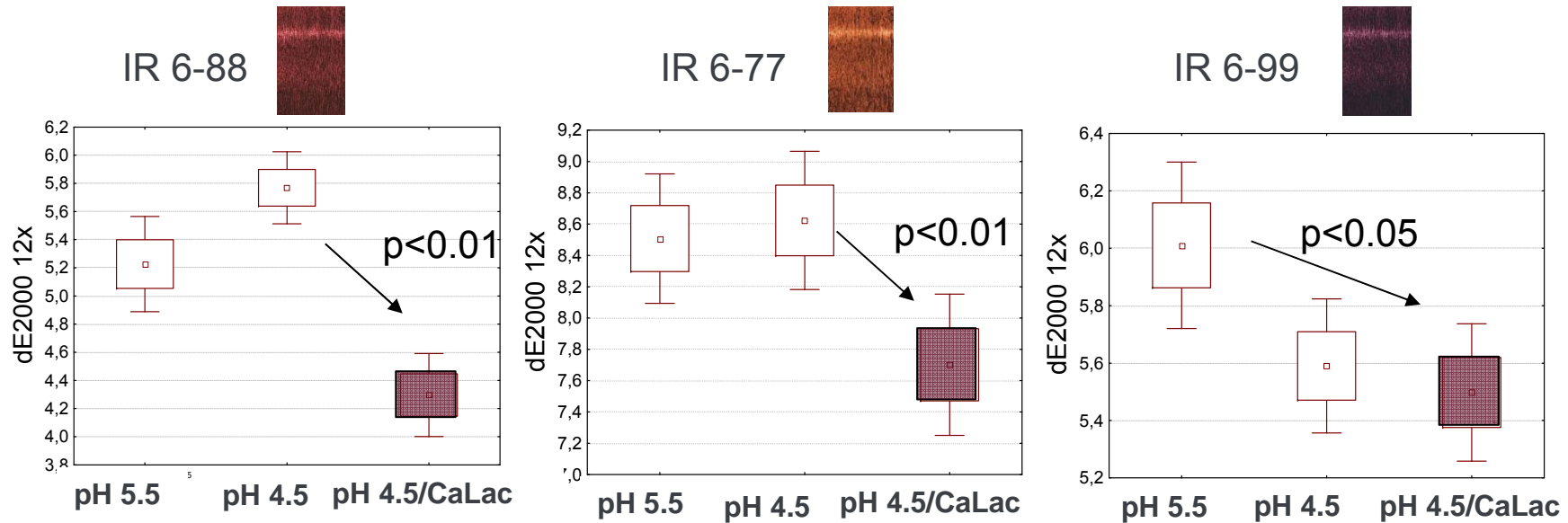
sham. pH 4.5
tartaric acid 2%

sham. pH 4.5
malic acid 2%

sham. pH 4.5
lactic acid 2%

Ionic-Modification of Matrix

Influence of oxidative hair color



- Effects based on pH depend strongly on the hair color
- Ca lactate shows an increase of color retention on all tested shades

Ionic-Modification of Matrix

Hand washes with commercial shampoos

- hair strands after 12 hand washes with commercial shampoos

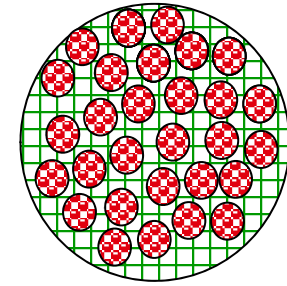


without Ca lactate at pH 4.75



with Ca lactate at pH 4.5

Conclusion



- The amorphous matrix is the key target of the inner hair structure for cosmetic treatments
- Oxidative treatments lead to unstable matrix conditions
- Ionic induced matrix modification can re-stabilize the inner hair structure and improve the retention of oxidative colors at the same time
- Hair treatments of pH 4.5 show a maximum effect on bleached hair
- The color retention strongly depends the choice of organic acid and the ions
- Strong effects could be found for **Ca lactate**