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pH evolution in solution after contact with multilayer films after different g- irradiation doses and thus reconciliation of pH and TOC with carboxylic acids detected by ion chromatography

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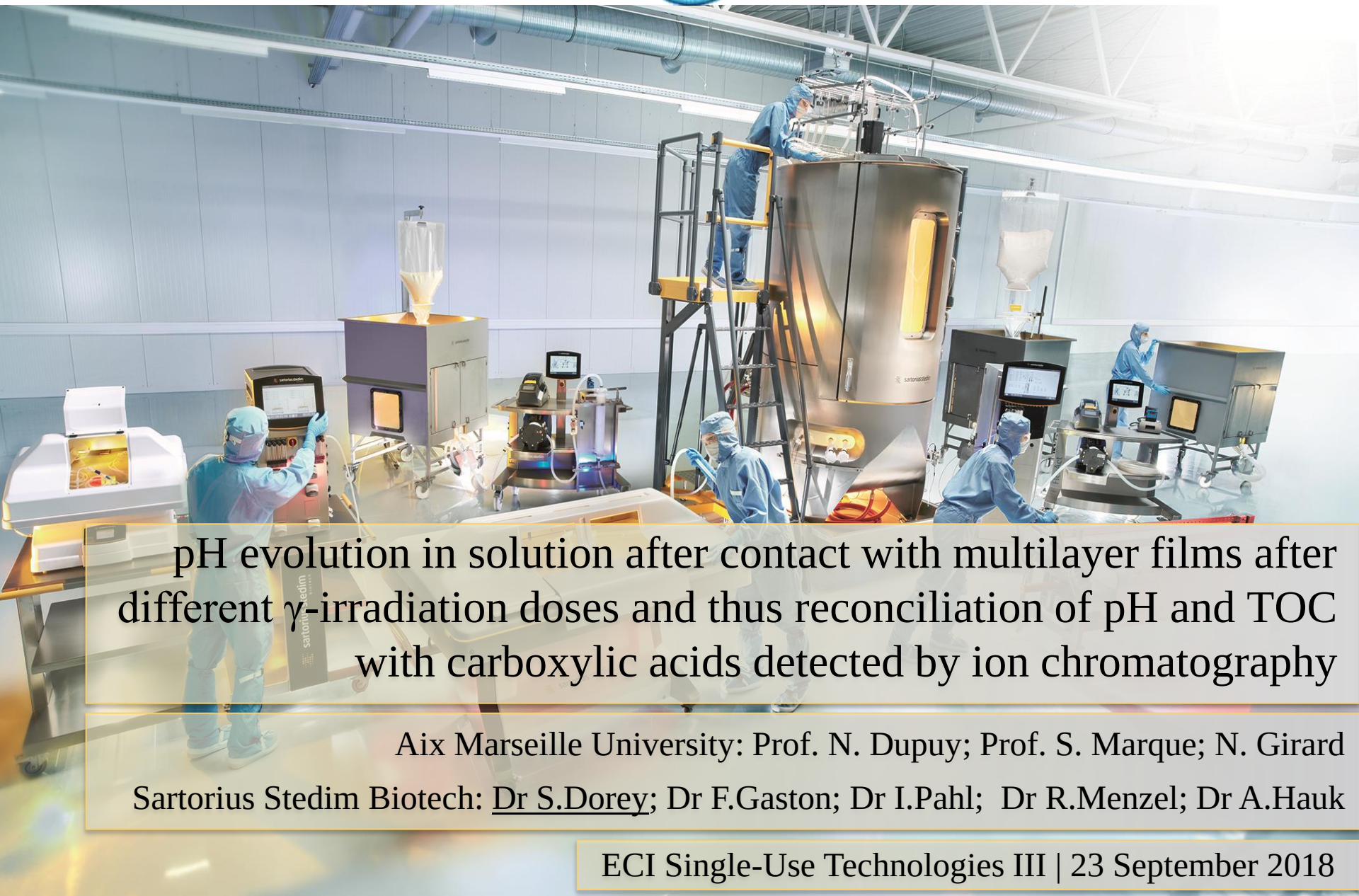

pH evolution in solution after contact with multilayer films after different γ-irradiation doses and thus reconciliation of pH and TOC with carboxylic acids detected by ion chromatography

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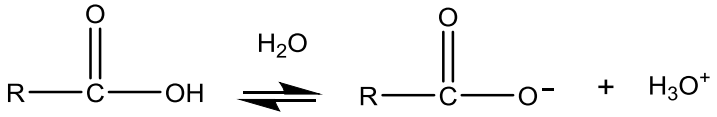
Purpose and scope

- Chemicals transfers can occur between plastic containers and contents
- pH and conductivity shifts can be observed in solutions in contact with SUS
- Organic species released among which carboxylic acids released

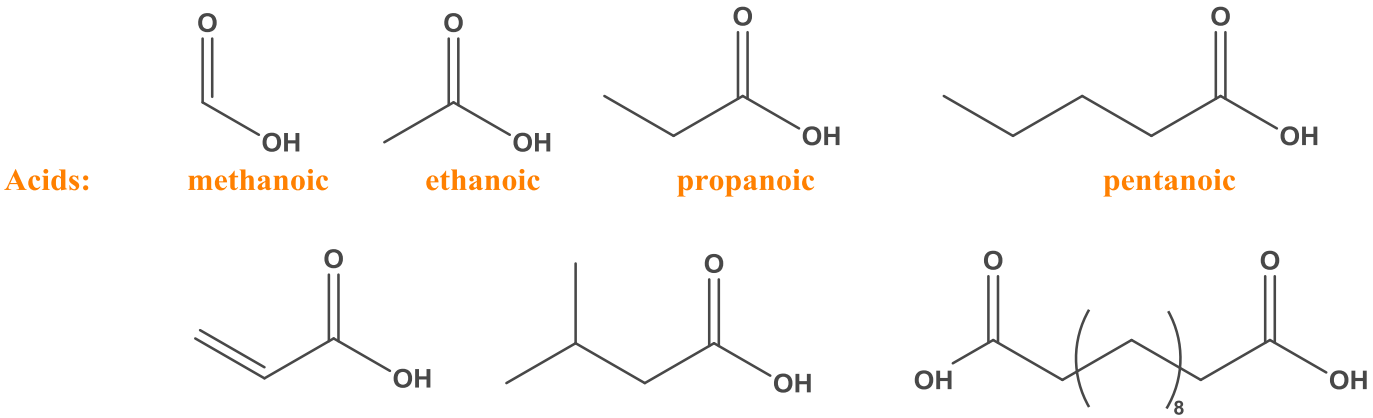
→ How carboxylic acids are generated? How can we specifically detect them? Can we anticipate their formation and their quantity? Can we predict associated observations linked to the release of carboxylic acids? Can we reconcile the pH measurements with other E&L analytical methods?

What is a carboxylic acid?

- Carboxylic acid is an organic compound in which a carbon (C) atom is bonded to an oxygen (O) atom by a double bond and to a hydroxyl group (−OH) by a single bond[1]



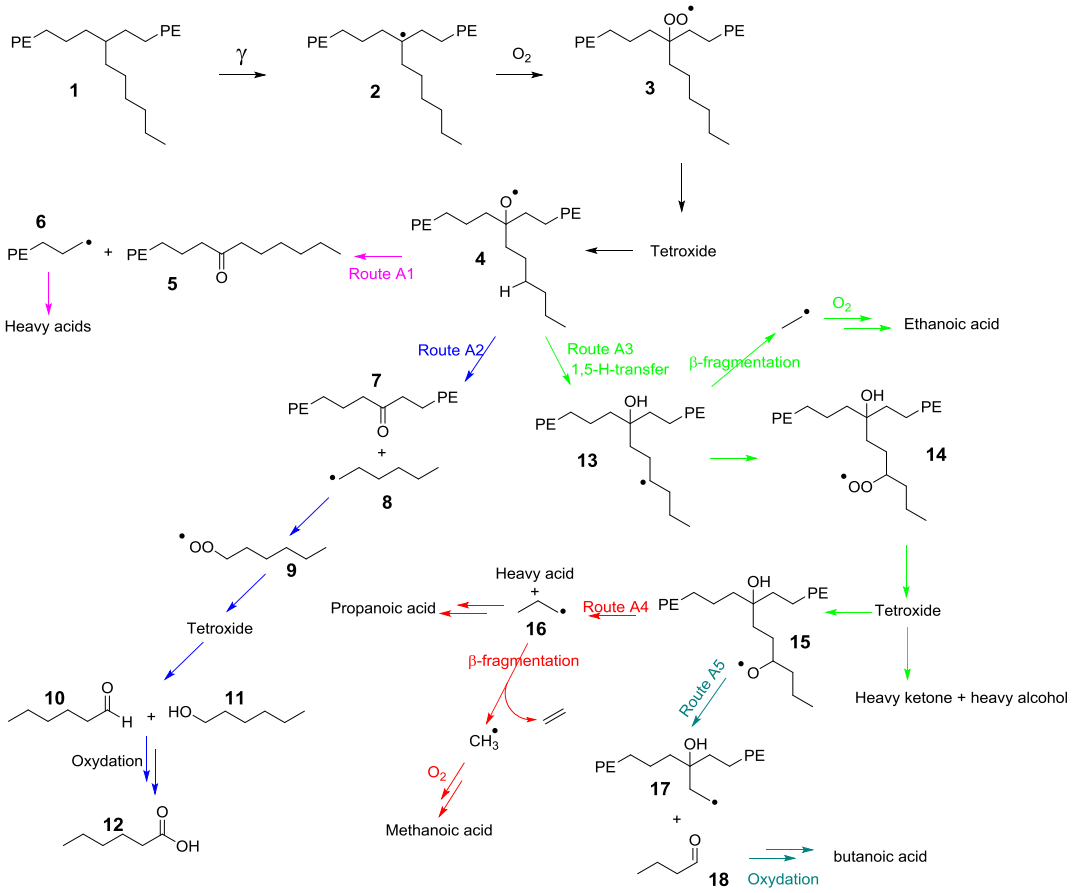
- Some frequent carboxylic acids and their chemical structures:



(1) Shang-Tian Yang, Hanjing Huang, Abdullatif Tay, Wei Qin, Lucita De Guzman, Ellen C. San Nicolas, Chapter 16 - Extractive Fermentation for the Production of Carboxylic Acids, Editor(s): Shang-Tian Yang, Bioprocessing for Value-Added Products from Renewable Resources, Elsevier, 2007, Pages 421-446

Formation of oxygenated species from polyethylene copolymers (1)

- γ-irradiation induces physico-chemical reactions in polymers



(1) Samuel Dorey, Fanny Gaston, Nathalie Dupuy, Magali Barbaroux, Sylvain R.A. Marque, Reconciliation of pH, conductivity, total organic carbon with carboxylic acids detected by ion chromatography in solution after contact with multilayer films after γ-irradiation, European Journal of Pharmaceutical Sciences 117 (2018) 216–226

Formation of oxygenated species from polyethylene copolymers (1)

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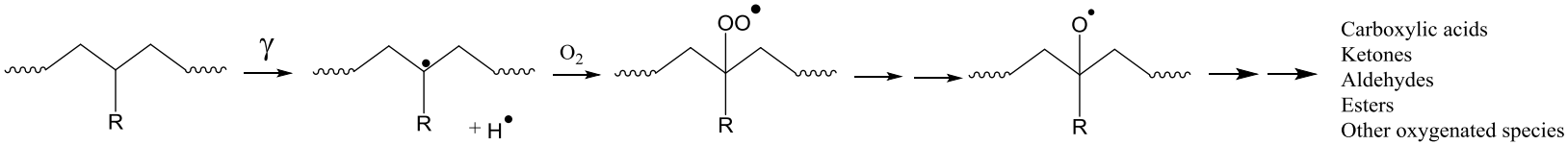
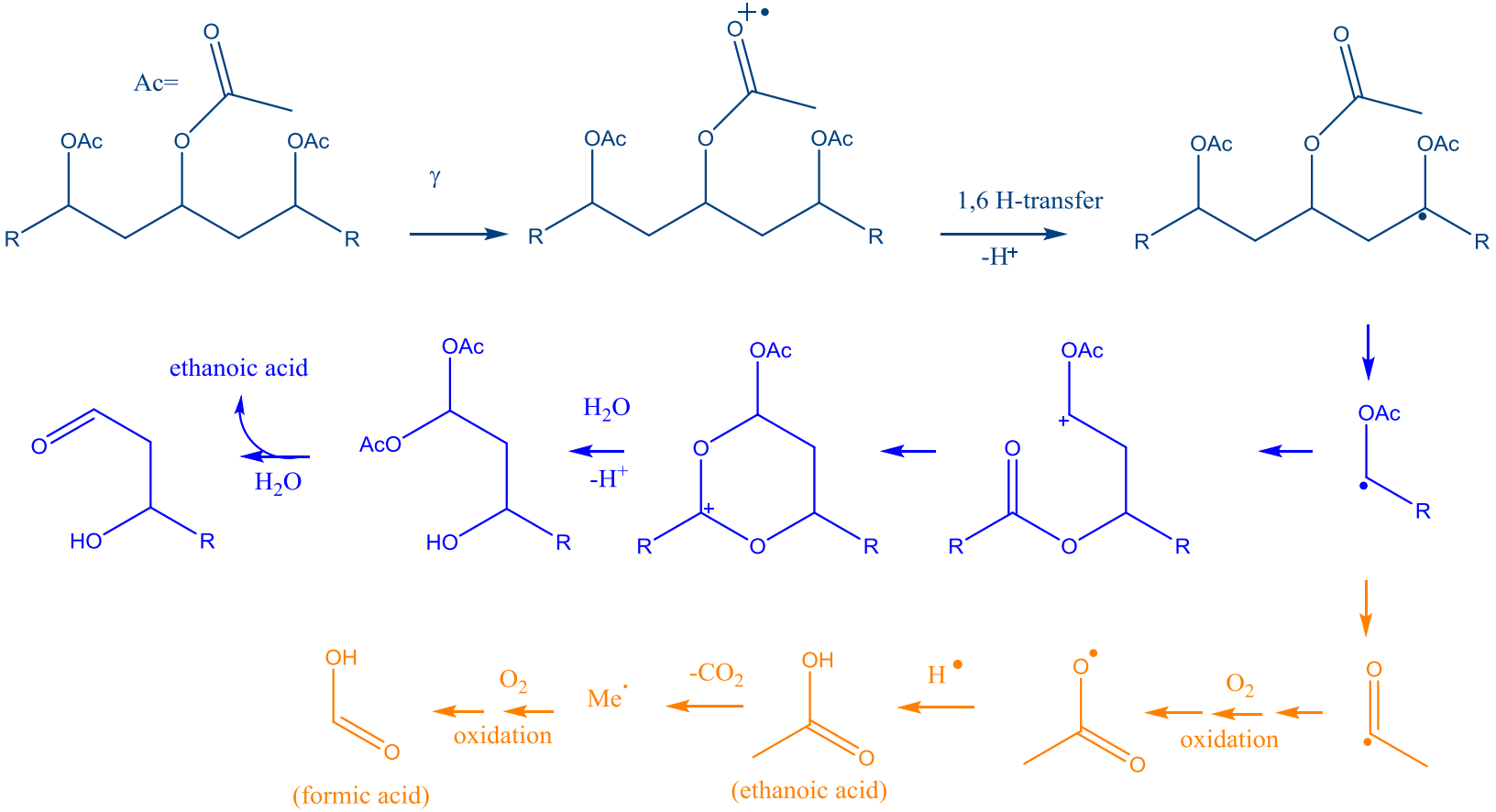


(1) Samuel Dorey, Fanny Gaston, Nathalie Dupuy, Magali Barbaroux, Sylvain R.A. Marque, Reconciliation of pH, conductivity, total organic carbon with carboxylic acids detected by ion chromatography in solution after contact with multilayer films after γ-irradiation, European Journal of Pharmaceutical Sciences 117 (2018) 216–226

Formation of oxygenated species from EVA (polyethylene-vinyl acetate copolymers)



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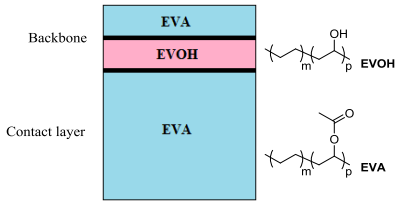
Protocol overview

Influence of film type and thickness	Influence of gamma irradiation dose	Storage time (40°C, 6 cm²/mL)	Analysis
	0 kGy	1 day	pH
	30 kGy	7 days	Conductivity
	50 kGy	21 days	TOC (Total Organic Carbon)
	115 kGy	70 days	Ion chromatography (IC)
	270 kGy	120 days	

EVA Film

Measurements

Ion Chromatography (IC) measurements:

Carbon atoms	Common name	IUPAC name	pKa (1)
1	Formic acid	Methanoic acid	3.74
2	Acetic acid	Ethanoic acid	4.76
3	Propionic acid	Propanoic acid	4.88
3	Acrylic acid	Prop-2-enoic acid	4.25
3	Lactic acid	2-Hydroxypropanoic acid	3.86
4	Butyric acid	Butanoic acid	4,82
4	Isobutyric acid	2-Methylpropanoic acid	4.86
4	Maleic acid	(2Z)-But-2-enedioic acid	1.83/6.59
5	Valeric acid	Pentanoic acid	4.82
5	Isopentanoic acid	3-methylbutanoic acid	4.8
6	Caproic acid	Hexanoic acid	4.88

(1) [i] Y. Zeng, X. Chen, D. Zhao, H. Li, Y. Zhang, X. Xiao, Estimation of pKa values for carboxylic acids, alcohols, phenols and amines using changes in the relative Gibbs free energy, Fluid Phase Equilibr. 313 (2012) 148-155.
[ii] M. Namazian, S. Halvani, Calculations of pKa values of carboxylic acids in aqueous solution using density functional theory, J. Chem. Thermodyn. 38 (2006) 1495-1502.
[iii] S.J. Gluck, K.E Steele, M.H. Benkö, Determination of acidity constants of monoprotic and diprotic acids by capillary electrophoresis, J. Chromatogr. 745 (1996) 117-125.
[iv] H. Kahlert, F. Scholz, Acid-Base Diagrams, Springer, Germany 2013.

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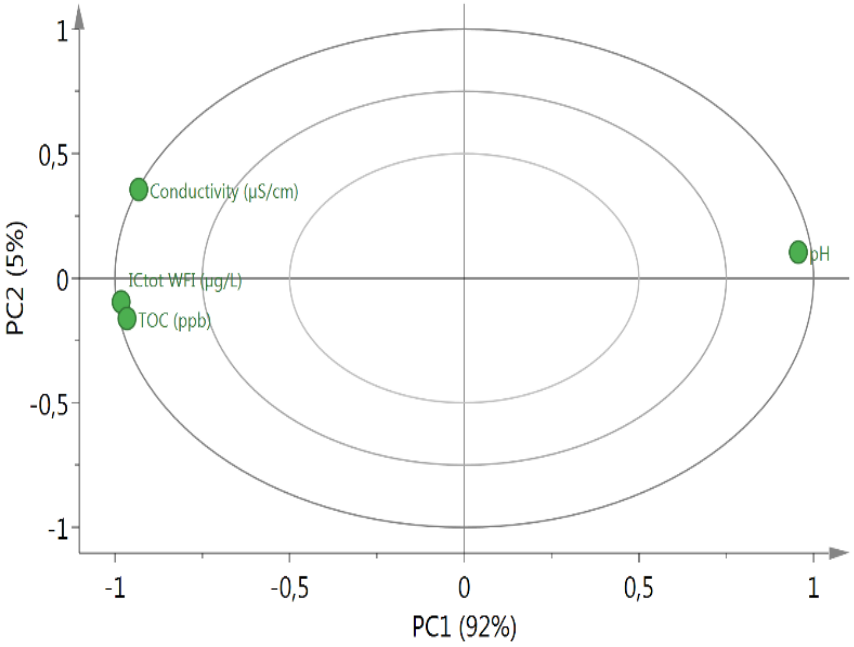
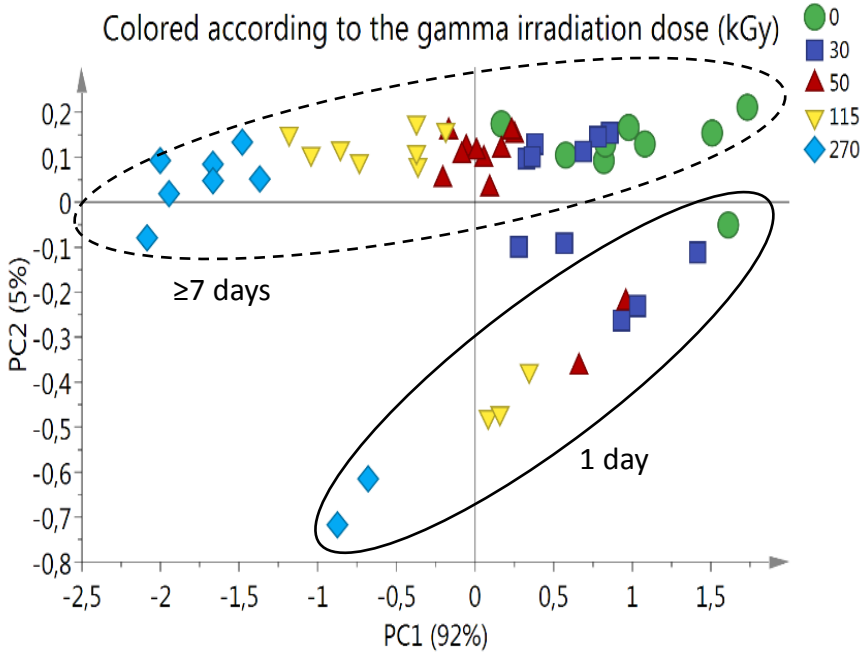
PCA analysis
EVA Film



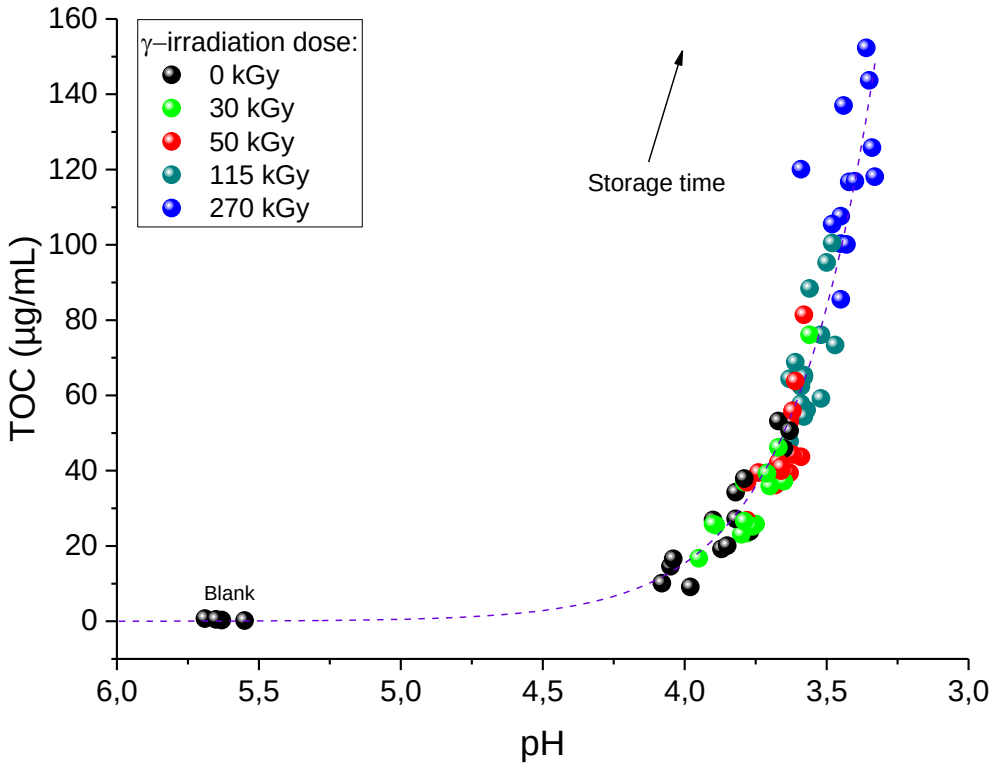


→ PCA shows a link between γ-irradiation dose & storage time with carboxylic acid generation and pH shift

→ Higher impact of the gamma irradiation vs the storage time with the EVA film

Evolution of the pH & TOC with the gamma irradiation dose

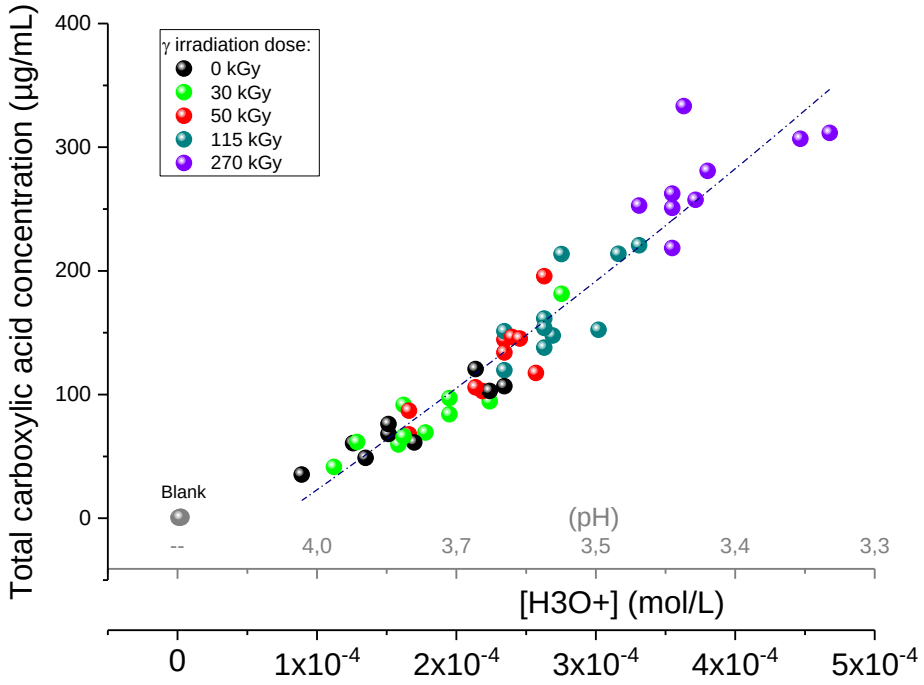
- **pH and TOC are measured in solutions in contact with films after different γ-irradiation dose**



→ pH decreases and TOC increase proportionality with the γ-irradiation dose

Evolution of acid concentration with the gamma irradiation dose

- **All carboxylic acids monitored by IC (Ion Chromatography) in solutions in contact with films after different γ-irradiation dose are sum up – NB: $[H_3O^+] = 10^{-pH}$**



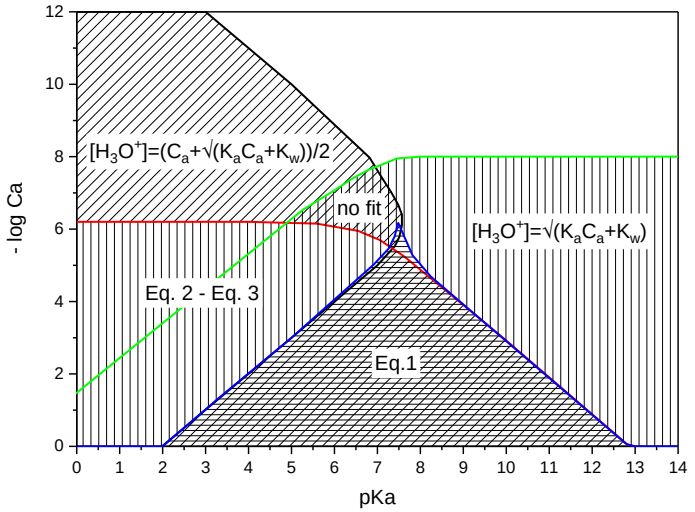
→$[H_3O^+]$ and IC_{tot} increase proportionality with the γ-irradiation dose

→$[H_3O^+]$ and IC_{tot} tightly clustered and proportional indicates there is a relationship

Can we predict pH, TOC, and conductivity from IC data?

Prediction of the pH from IC data

- **Applying the approximation formulae in the acid-base equilibria[1]**



Equation 1: $[H_3O^+] = \sqrt{K_a\, C_a}$

Equation 2: $[H_3O^+] = \frac{-K_a + \sqrt{K_a^2 + 4KaCa}}{2}$

Equation 3: $[H_3O^+] = \frac{-K_a + \sqrt{K_a^2 + 4K_a(C_a - \alpha)}}{2}$

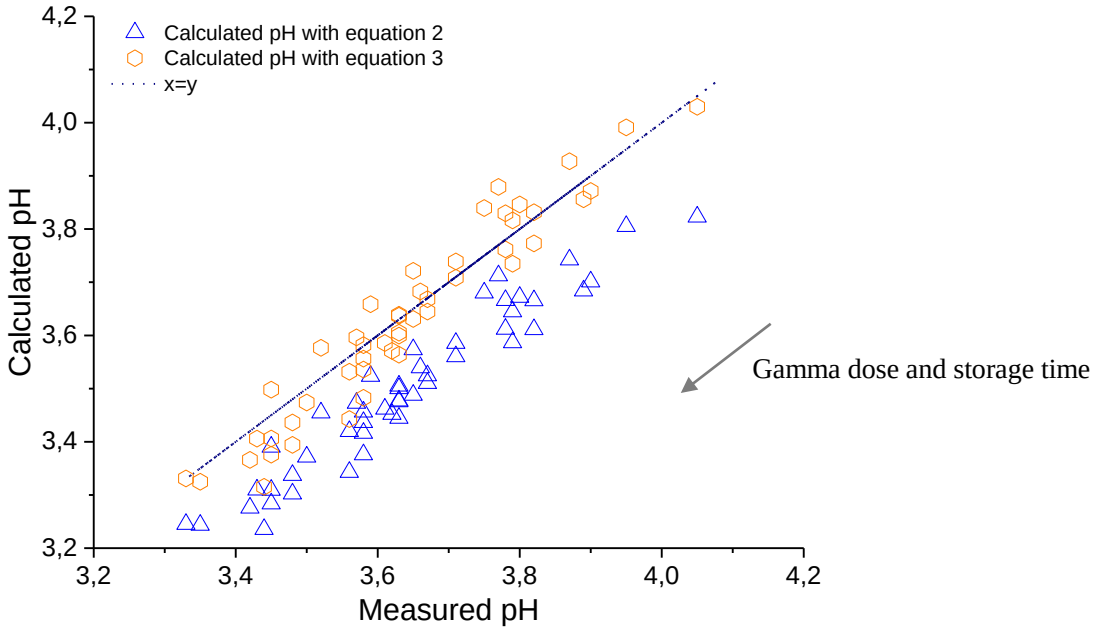
Equation 4: $K_a = \frac{\alpha(\alpha + 10^{-7})}{C_a - \alpha}$

- $[H_3O^+]$ = concentration of H_3O^+
- K_a = dissociation constant
- C_a = concentration of each acid
- α = dissociation coefficient
- K_w= water dissociation constant

(1) *NARASAKI*, H. *1987.* "The range of application of the approximation formulae in acid-base equilibria," *Fresenius Z. Anal. Chem., 328: 633-638*

Prediction of the pH from IC data

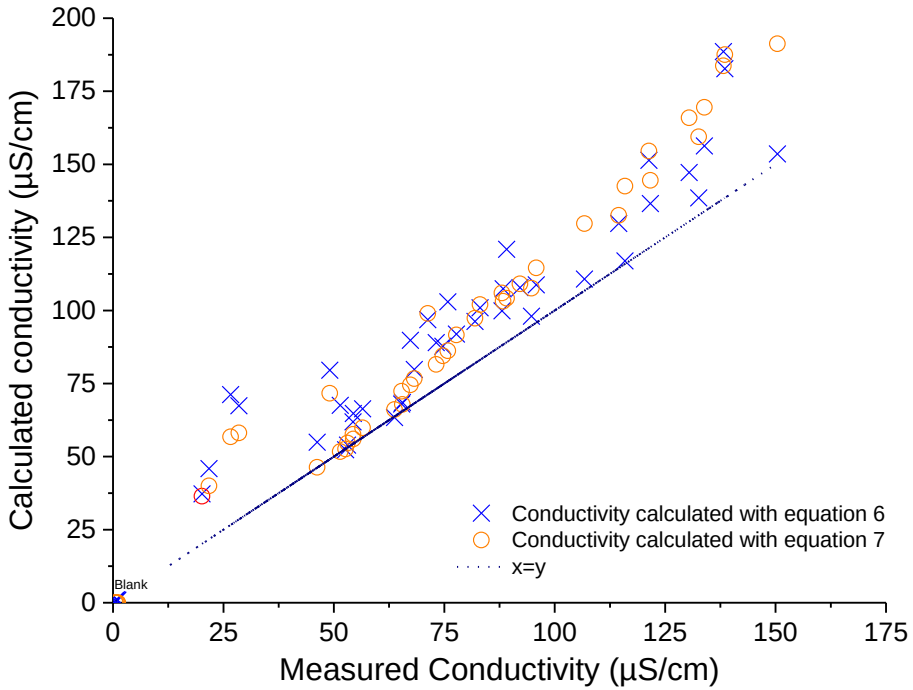
- **pH data calculated from each acid concentration**
- pH calculated from each acid concentration with equation 1 gave erroneous values (not plotted)



→ pH values can be predicted (calculated) from IC data

Prediction of the conductivity from IC data

- **Conductivity data calculated from each acid concentration**



The conductivity can be expressed as:

Equation 5: $\text{Conductivity} = \sum z_i \lambda_i . [X_i]$

Equation 6: $\sum z_i \lambda_i . [X_i] = z_i \lambda_i [H_3O^+]_{measured} + \sum z_i \lambda_i [RCOO_i^-] = 10^{-pH_{measured}} + \sum z_i \lambda_i [H_3O_i^+]$

Equation 7: $\sum z_i \lambda_i . [X_i] = z_i \lambda_i [H_3O^+]_{calculated} + \sum z_i \lambda_i [RCOO_i^-]$

- [Xi] = concentration of each carboxylic acid
- $[H_3O^+]$ = concentration of H_3O^+
- λ_i = molar electrolytic conductivity (in $S.cm^2.mol^{-1}$)
- z_i = ionic charge

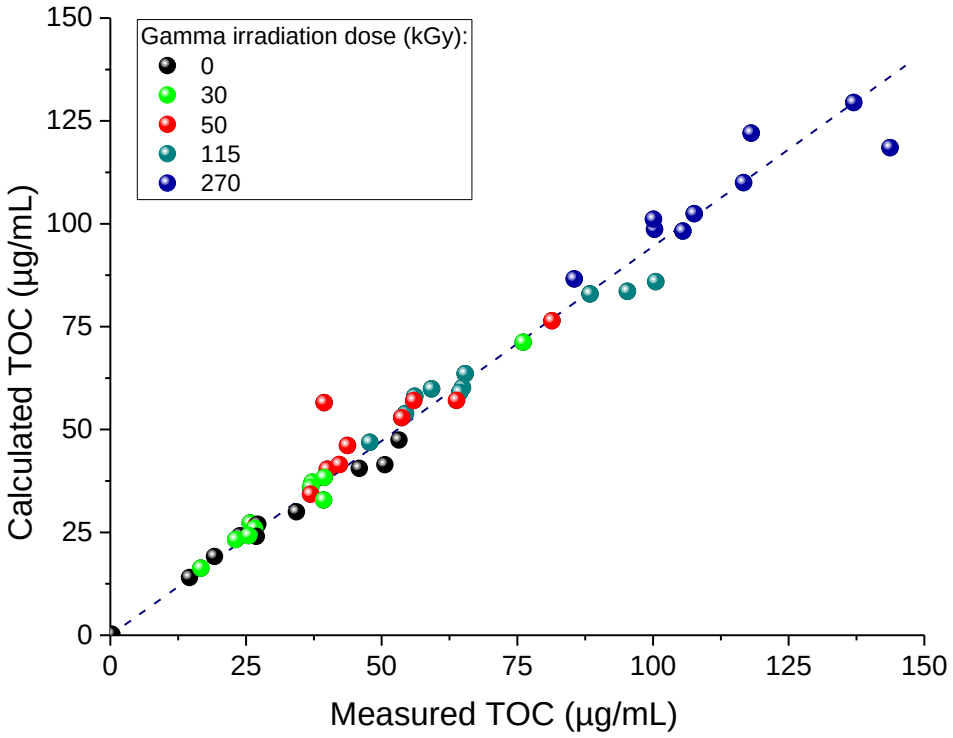
→ Conductivity values can be predicted (calculated) from IC data

Prediction of the TOC from IC data

The TOC_{IC} is calculated from IC data:

$$TOC_{IC} = \sum C_i \cdot \frac{M_{c_i}}{M_{w_i}} = \sum C_i \cdot \frac{n_{c_i} \cdot m_c}{M_{w_i}}$$

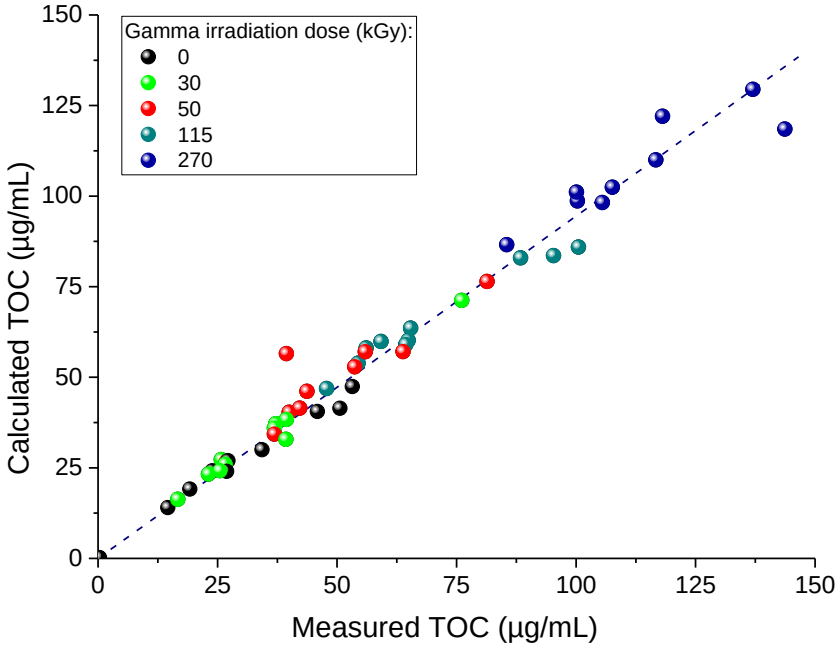
- i = each carboxylic acid
- M_{Ci}=mass of carbon in i
- m_c=molar mass of carbon
- n_{Ci}=number of carbon atoms in i
- C_i =concentration of the carb. acid i
- M_{Wi}=molar mass of i

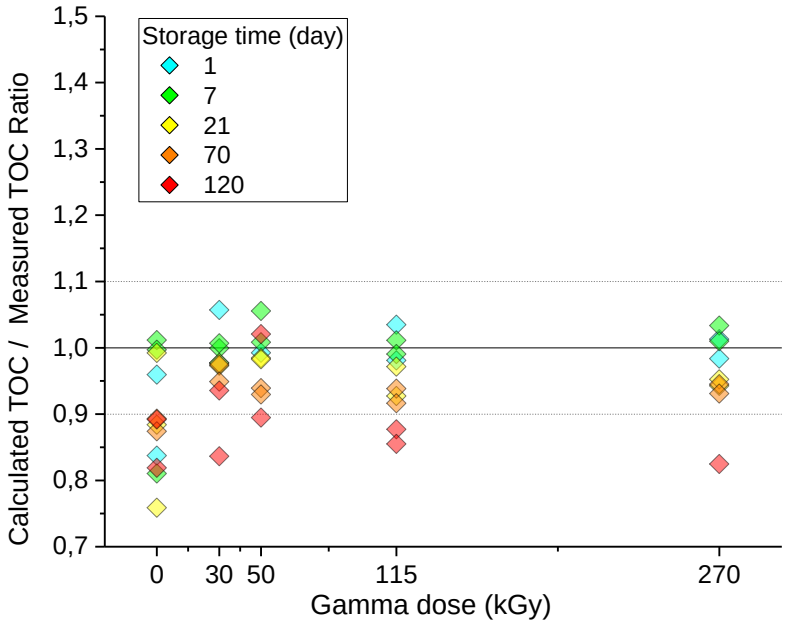


Prediction of the TOC from IC data

- **Calculation of carbon quantity (TOC_{IC}) from IC**
- **Ratio "calculated TOC_{IC} vs measured TOC" considered**

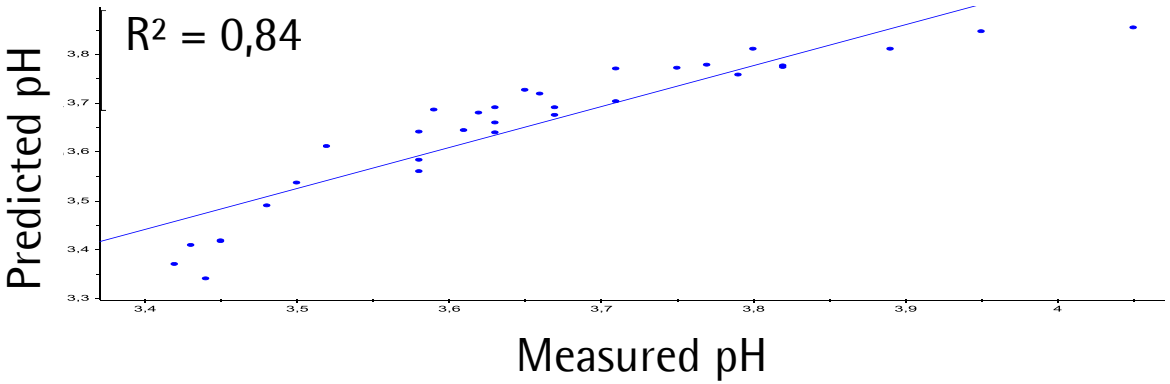
  → Ratio always close to one at short contact time



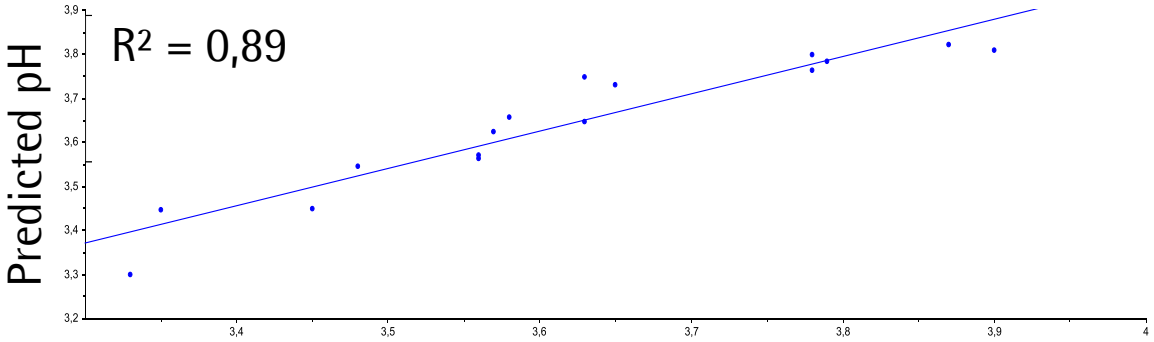


Prediction of the pH from IC data with PLS

- **Use of chemometrics (PLS) to predict the pH from IC**



Calibration Model



Prediction

→ pH values can be predicted from IC data with PLS

Contents

Conclusion

- **Polyolefins (PE, PP, EVA, etc.) are prone to generate carboxylic acids during gamma irradiation**
- The extent of the carboxylic acid generation & release depends on the polymer
- The carboxylic acid release should be counter-balanced by appropriate buffer concentration according to the couple polymer nature | γ-irradiation dose
- **Carboxylic acids not easily detected by (HS)-GC-MS; IC can do**
- Reconciliation of pH, conductivity and TOC with IC data in pure water and possibility to predict them
- Beyond the E&L measurement: possibility to extrapolate the E&Lprofile obtained in pue water to other solvents → See our poster for details and example

Questions and Discussion