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The key role of non-volatile organic acids in historical paper

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Results and Discussion

Acetic acid, which is emitted from paper and is often considered as a pollutant, was present in all the examined sacrificial historical papers (Fig. 1). The surprise was oxalic acid, which was present in the highest concentrations and in a clear correlation with the pH of acidic paper (Fig. 2). It can thus be considered as the driver of acid-catalysed hydrolysis, a key process of paper degradation. Since, unlike acetic acid, oxalic acid is not volatile and is also more acidic (Tab. 1), the research indicates that the role of acetic acid in the degradation of paper is minimal and that it does not pose a risk as a contaminant in paper collections. As oxalic acid can be effectively neutralised with calcium or magnesium bases (Tab. 2), its effect on paper degradation can be significantly reduced by deacidification with agents containing Ca²⁺ or Mg²⁺ ions.



Fig. 1: Content of organic acids in paper samples.

Tab. 1: Acidity and volatility of selected organic acids.			
	Oxalic acid dicarboxylic	Acetic acid	Formic acid
рКа	1.25 4.14	4.76	3.75
Vapour presssure [mm Hg] at 25 °C	0.001	15.7	42.59
Tab. 2: Solubility of Ca and Mg salts of selected organic acids.			
SOLUBILITY in water	Oxalate	Acetate	Formate
Ca ²⁺	6.1 mg/L	347 g/L	161 g/L
Mg ²⁺	0.38 g/L	534 g/L	144 g/L



Fig. 2: Effect of oxalic acid content on paper pH. The ellipse delineates the group of samples with a pH over 6.5.

Conclusions:

- Oxalic acid is responsible for decrease of paper pH during natural ageing
 - increase of OX 0.01 mmol/g of paper resulting in a decrease in pH of 0.008
- Strong corelation between oxalic acid and lignin content indicating lignin as the major source of oxalic acid
- Oxalic acid is not the pollutant in archival air, but can contributes to protonation of acetic and formic acid

References

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