IAQ2003

Sulfur and Nitrogen in Collagen

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Key points

- This research involves the study of oxidative mechanisms in gelatin used as a surrogate for museum collagen artefact degradation.
- Many artefacts are composed or contain collagen: leather, parchment, gelatin binders (photographic film, Baroque marble).
- Gelatin, modern leather and parchment have been used to the study the oxidation of S(IV) SO_2 and N(IV) NO_2,
- Metal contents of modern, historic leather and parchment will influence reaction rates and hence degradation.
- The deposition of sulfur dioxide and nitrogen dioxide to thin layers of leather is dependent on the rate of oxidation within the material. The above transform to sulfuric, nitrous and nitric acids which are very detrimental.

Offenbach leather museum

Germany

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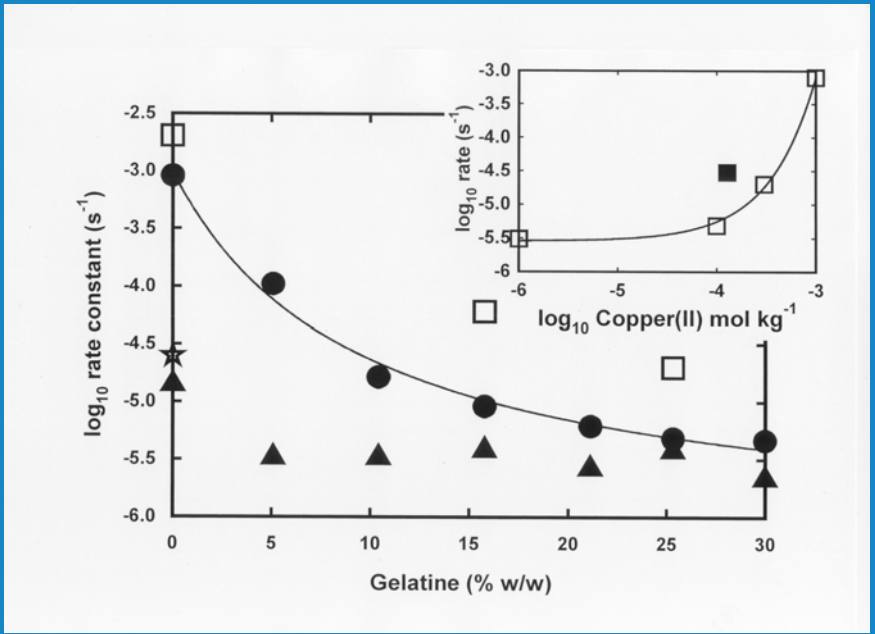
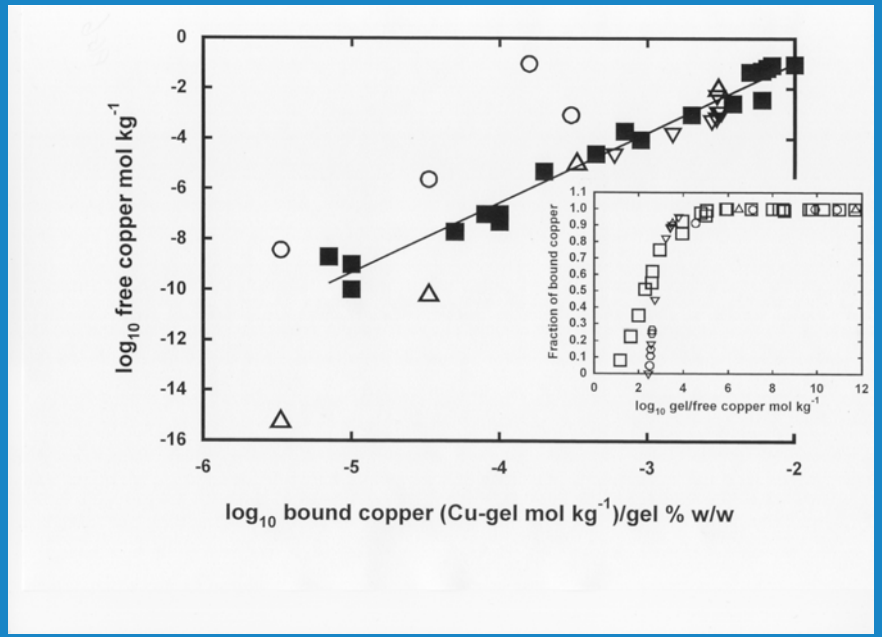
Leverhulme Trust Grant

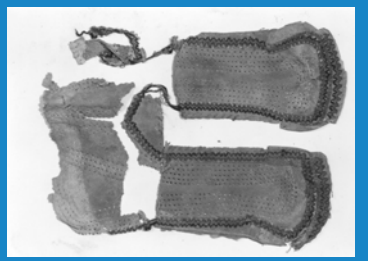
The Rate of Metal Catalysed Oxidation of Sulfur Dioxide in Collagen Surrogates*



Rate constants for the oxidation of sulphur dioxide in gelatine at 25 ºC. Initial concentration of sulphur dioxide 1.27×10^{-3} mol kg^{-1} (molal) and pH of the received gelatine – 5.30, unless stated. *Triangles* – Gelatine slabs with no additional added metal, *Circles* – 1×10^{-4} mol kg^{-1} copper (II) – Cu^{2+}, *Open squares* – 3×10^{-4} mol kg^{-1} copper (II). *Star* – Pure water



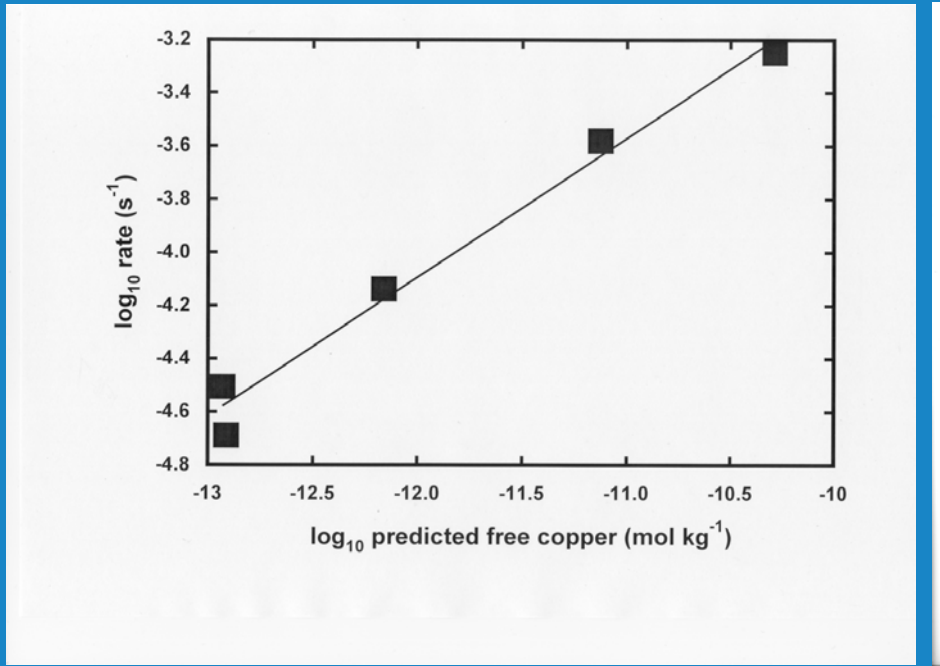
Free copper in collagen materials *Solid squares* - gelatine, *Triangle up* - parchment 30% w/w, *Triangle down* - parchment paste, *Circles* - silk 30% w/w.
Inset *graph* Fraction of bound copper.*Symbols* - as above + *Hexagons* - silk variable concentration (% w/w).

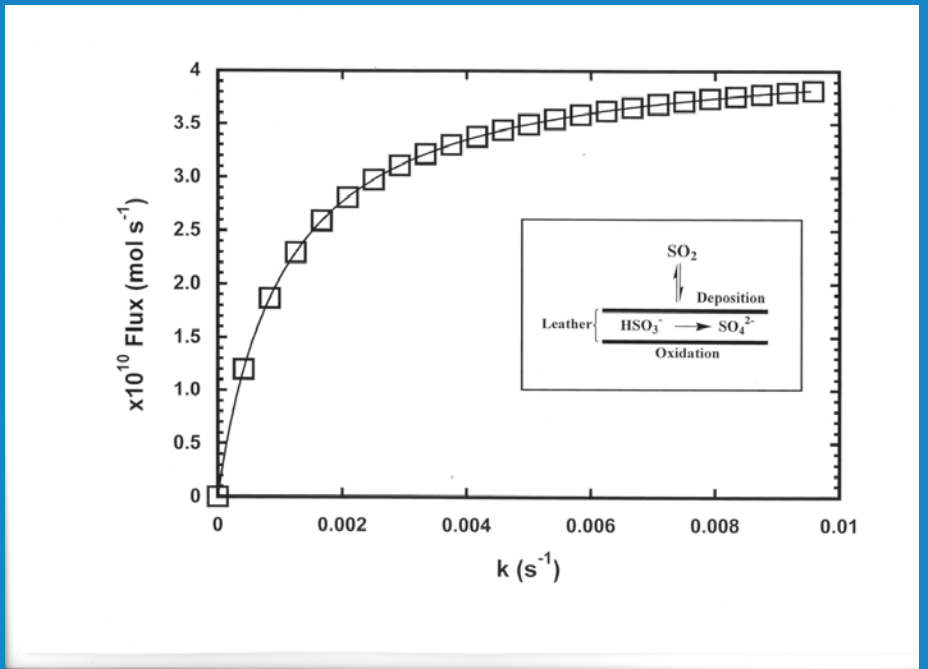


Copper pigmented leather Persian saddle cover - very degraded leather shrinkage temperature 25 °C!

*In press *Journal of Cultural Heritage* 2003

Sulfur in Collagen Continued...





The presence of free transition metal such as copper will increase the rate of oxidation of sulfur dioxide.

Deposition of sulfur to thin layers of leather depends on the rate of oxidation

The Oxidation of Nitrite in Gelatin as a Surrogate for Collagen based Artefacts

The air pollutant nitrogen dioxide (NO_2) can undergo many reactions within collagen typically:

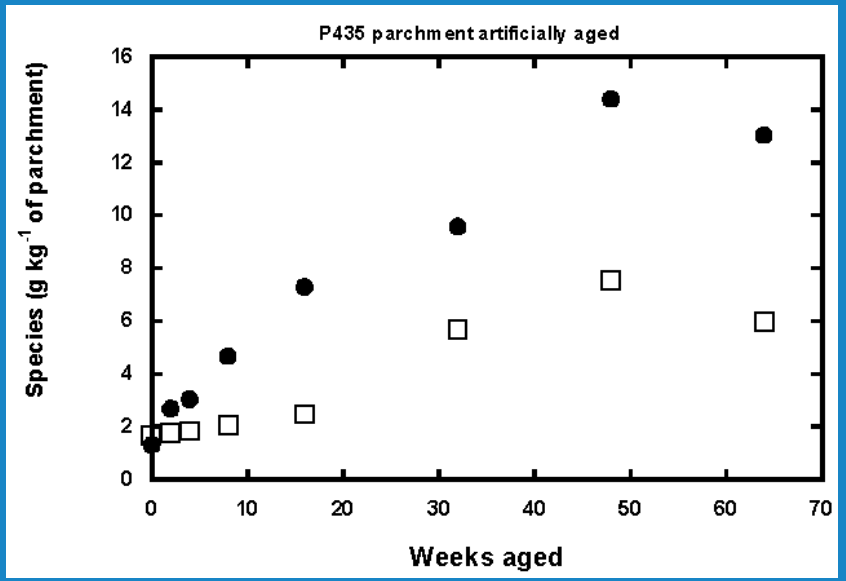
$$2NO_{2\,(g)} + H_2O_{\,(l)} \rightarrow HNO_{2\,(aq)} \text{ and } HNO_{3\,(aq)}$$

nitrous acid nitric acid

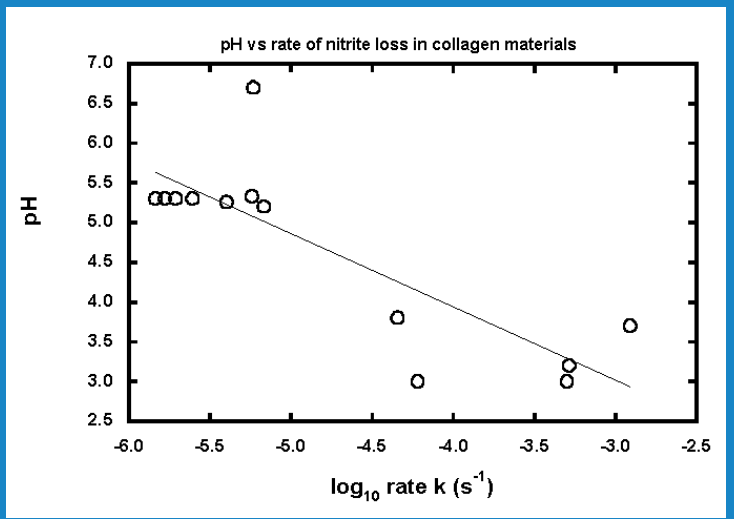
25.31% w/w gelatine no other additives	$1.677\times10^{-6}\ s^{-1}$
30.00% w/w sumac tanned leather	$5.210\times10^{-4}\ s^{-1}$
30.00% w/w mimosa tanned leather	$5.047\times10^{-4}\ s^{-1}$
30.00% w/w archival leather	$1.237\times10^{-3}\ s^{-1}$
30.00% w/w sheepskin parchment	nitrite present and increasing

For comparison:

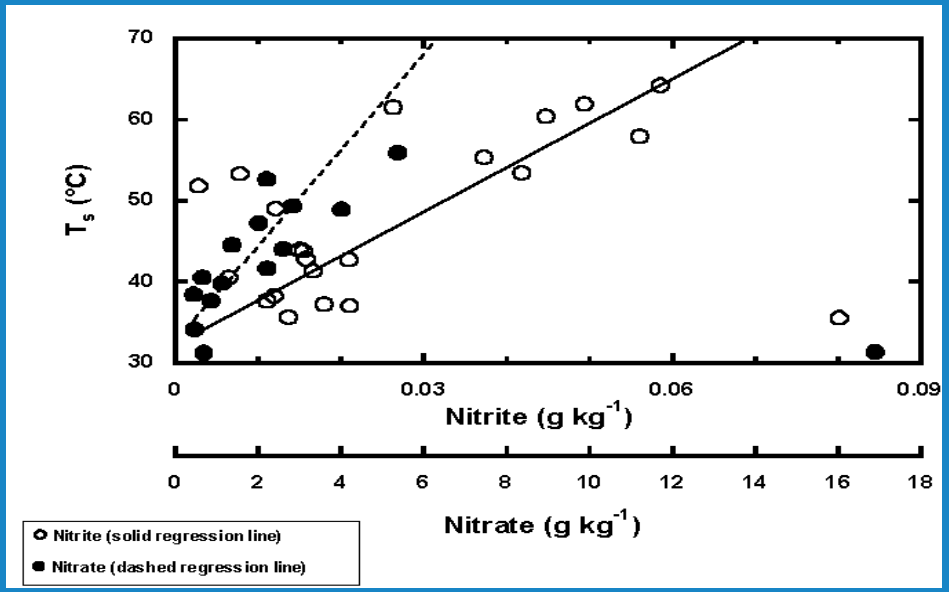
29.98 % w/w gelatin with sulfur dioxide	$2.16\times10^{-6}\ s^{-1}$



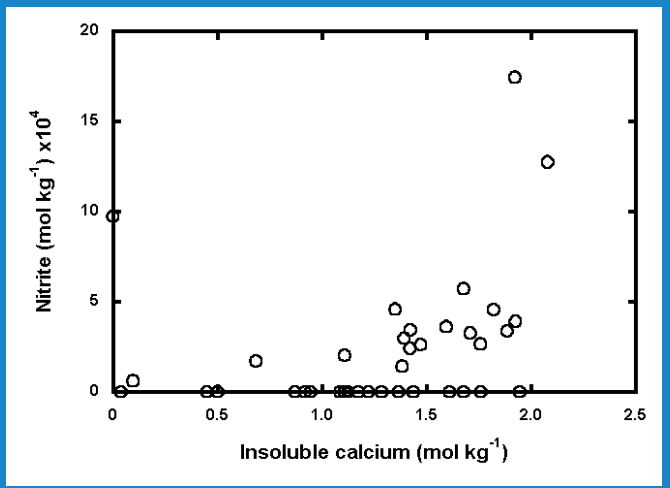
Circles - nitrate; Squares - nitrite

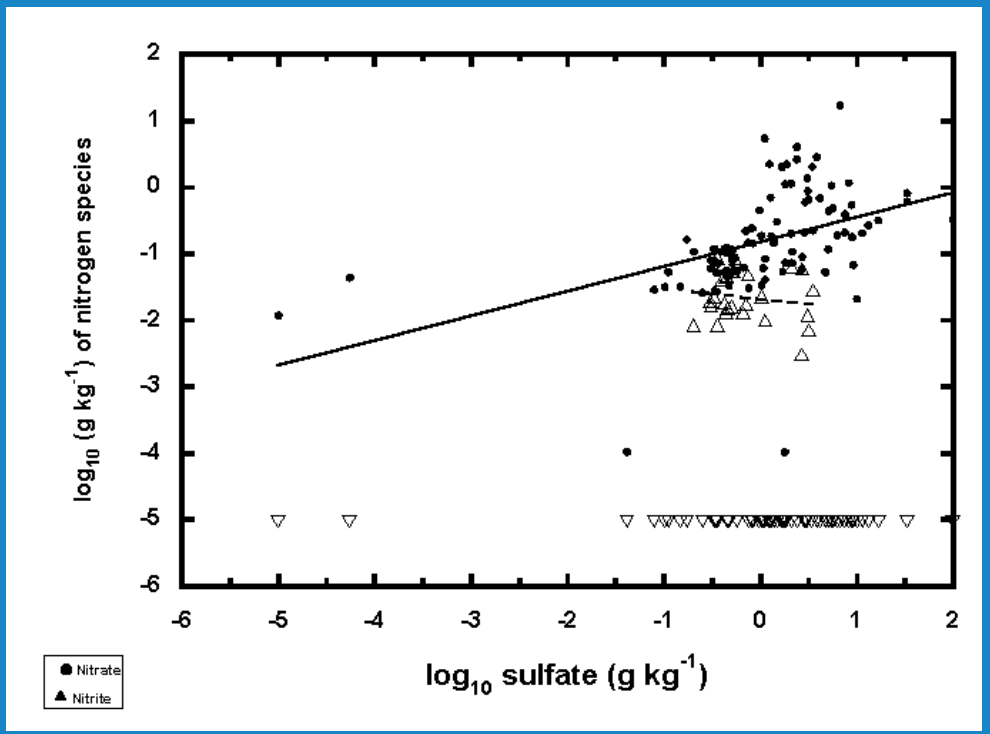


Nitrite in Collagen continued...

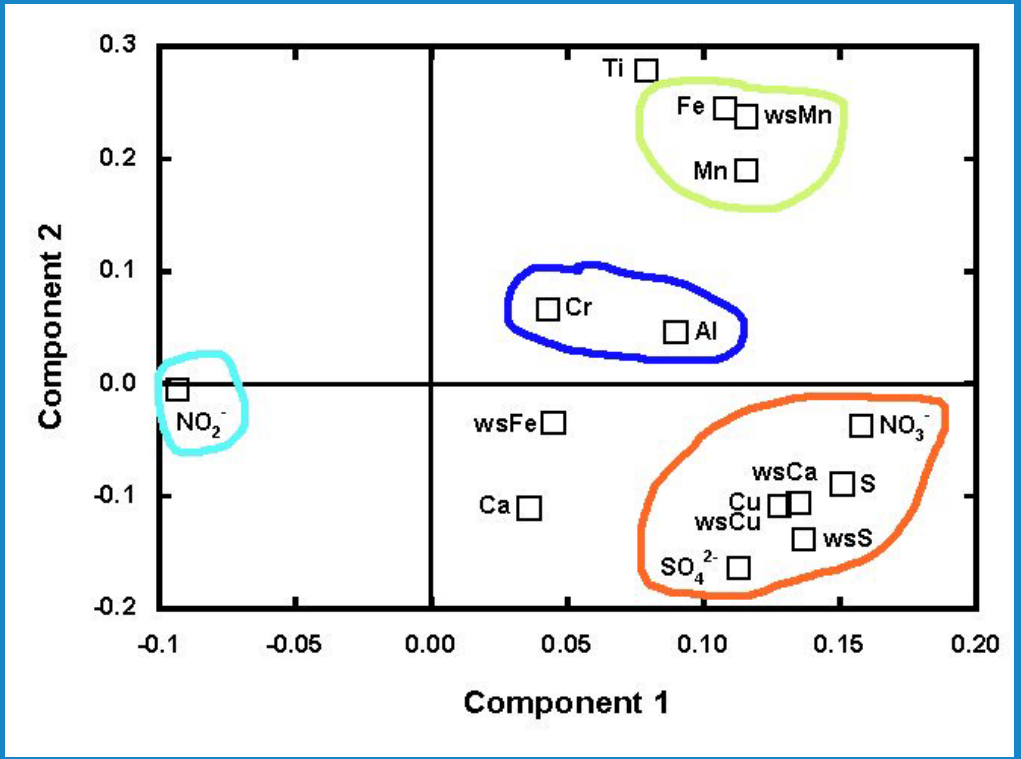


Historic parchment





Metal composition of historic leather and parchment



Historic parchment principle component analysis from analyses:

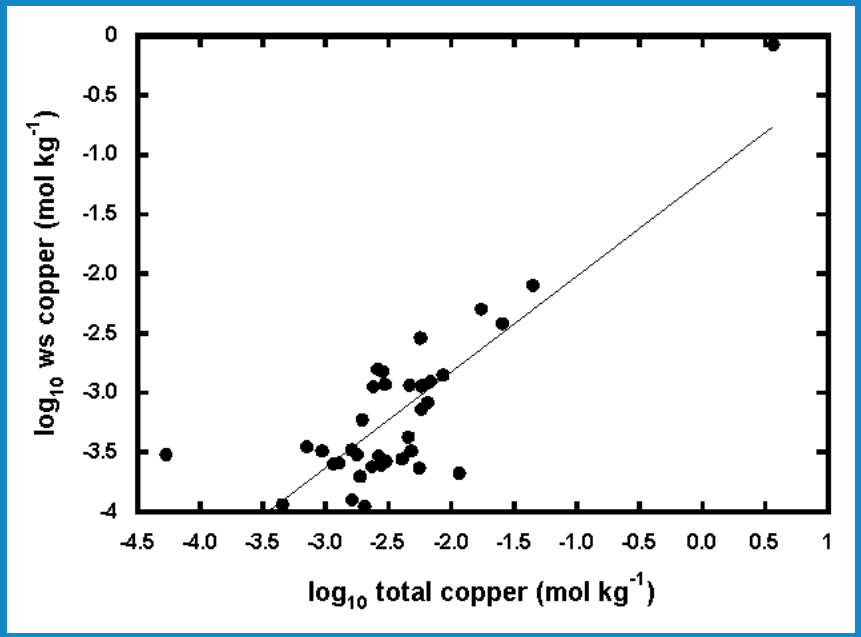
Green circled - typical catalysts naturally present.

Blue circled - possible additives

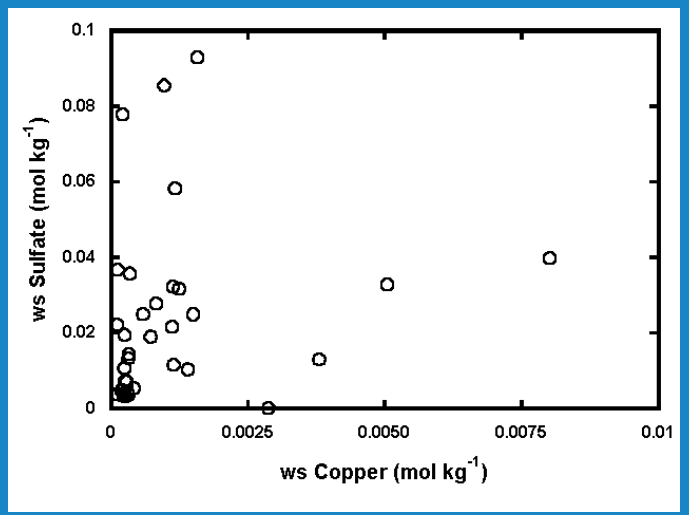
Red circled - acidic species occurring with copper a good catalyst, calcium mobilised.

Light blue - anomalous nitrite on its own.

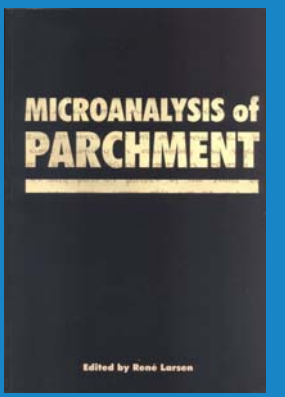
Metals continued…



Copper pigmented parchment



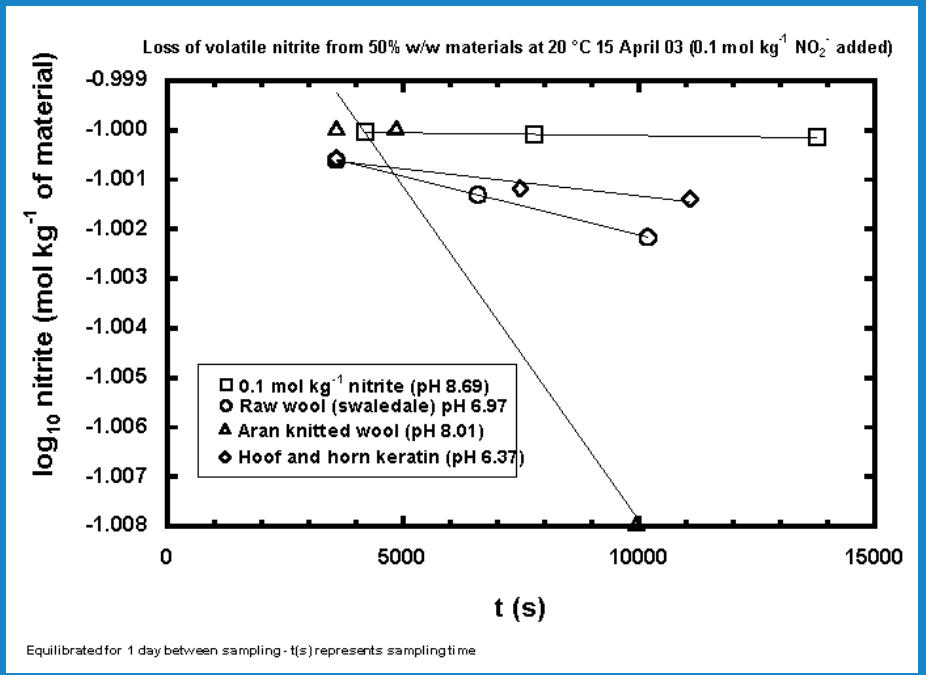
Historic parchment



Archetype Publications 2002

Emission of volatile nitrite (HONO or NO_2) from keratin†

Keratin, wool like parchment can contain 'natural' concentrations of nitrite and appears to produce it under certain conditions.



New materials

Sheep parchment	7.7×10^{-2} g kg^{-1}
Raw wool	1.5×10^{-3} g kg^{-1}
Aran spun wool	2.9×10^{-3} g kg^{-1}

† Currently investigating the kinetics of nitrite oxidation in keratin and stability of HONO within this matrix as part of the IMPACT project

http://www.bartlett.ucl.ac.uk/sustainableheritage/IMPACT_home.htm

IMPACT ('Innovative Modelling of Museum Pollution and Conservation Thresholds') is a European Commission Framework 5 research project

Conclusions

The oxidation rates of sulphur dioxide sulphuric acid are fast compared with the lifetime of objects. In gelatine the half-life of the dissolved SO_2 is 60 hours while in a sumac leather sample it was 79 hours.

Water content has little effect on the rate of SO_2 oxidation.

The oxidation is catalysed by free metal ions (e.g. Cu, Fe, Mn), but at typical metal concentration in collagens they would be bound and thus unavailable to act as catalysts. Only in leathers with high concentrations of metals, i.e. added as pigments, that free metal ions would be available to aid catalytic oxidation. The addition of copper to sheepskin cause little increase in rate of SO_2 oxidation indicating that it may rapidly become complexed in this system

The slow oxidation rate of S(IV) in collagens and gels limits deposition of sulphur dioxide gas. This means that additives in leathers that slow this rate may limit the sulphuric acid from absorbed sulphur dioxide.

Some collagen/protein like materials under certain conditions appear to contain or increase their nitrite concentration over time independent of air pollutants

Nitrate, sulfate, copper and water soluble calcium are related in historic parchment. Additives are easily spotted using principle component analysis (PCA). The relationships between other species and nitrite are harder to find as is the case when modern, historic leathers and parchments and other materials such as silk and tannins are investigated as a whole using PCA

Relating historic samples many with unknown pollutant exposure is difficult, however sulfate and nitrate are related, nitrite is partially related to insoluble calcium, water soluble copper is related to insoluble copper.