Russia Leather: Mysterious Process, Modern Chemistry

Method development for the analysis of tannins in leather artefacts

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Introduction

Russia Leather was a prestigious vegetable-tanned leather that was highly sought after for its superior properties (smell, colour and waterproofing). The exact 'recipe' for production was lost, but archival sources suggest that willow and birch barks were used as tanning materials. **Tannins** are an important element of leather production, but their analysis is difficult due to their complex nature. They are a class of network compounds that are built up of monomeric units, that have the ability to complex proteins. The action of tannins binding to the protein in skin (collagen) prevents degradation (**Fig. 1**).

Aim: Optimise an extraction method for tannins in leather and assess if the analysis of tannins by UPLC and FT-IR could be used in the identification of specific types of historically significant materials.

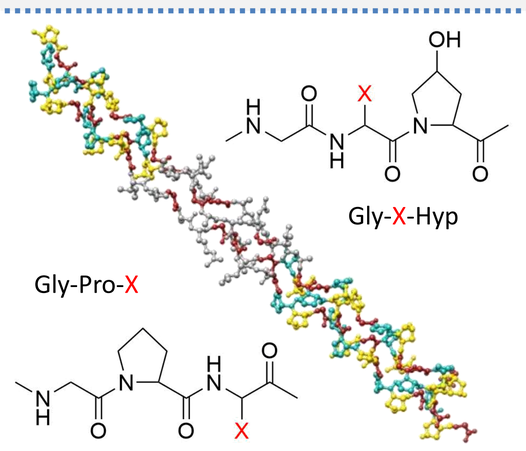
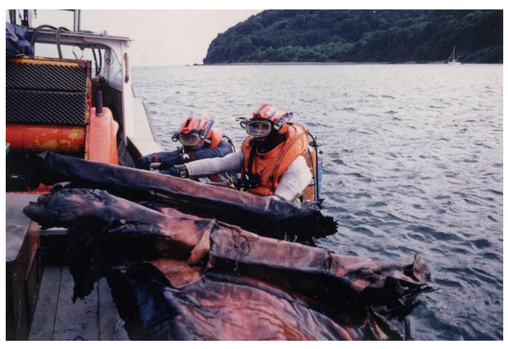


Fig. 1: 3D protein structure of collagen with the common amino acid motifs

X – any other amino acid



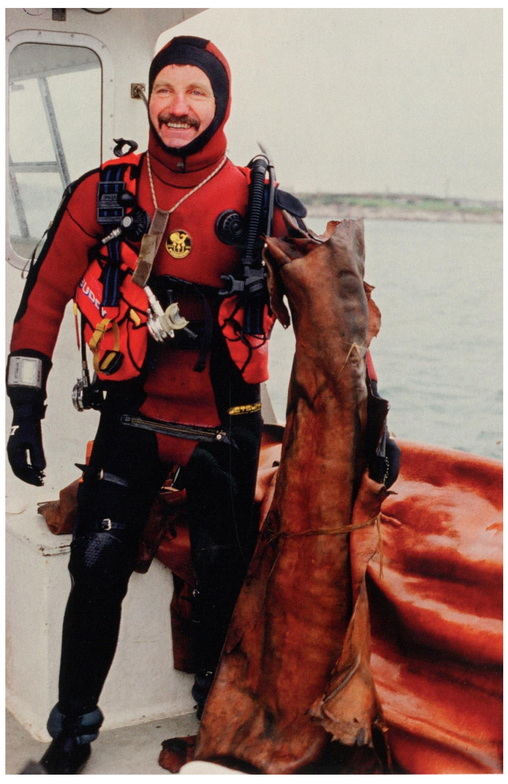


Fig. 2 & 3: Images from the excavation of the Metta Catharina (1972).

Samples

Reference Materials: Optimisation of extraction and hydrolysis were carried out on reference vegetable tanned leathers. The UPLC gradient and separation was evaluated using a mixture of 12 pure chemical standards (tannins, flavonoids and anthraquinones).

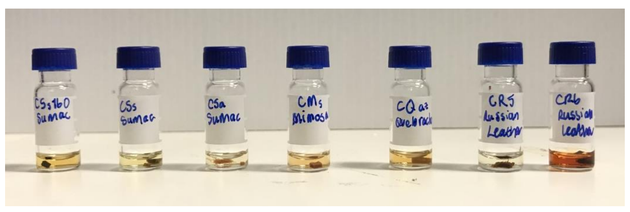


Fig. 4: Extracts of reference materials.

Fig. 5 *Russia leather* samples analysed in this research: **(1 - CR5)** Metta Catharina von Flensburg, **(2 - CR1**, 5 - **CR2)** Juktenskobben, **(3 - CR3)** St Nicholas, **(4 - CR4)** Texel.

Table 1: The *Russia Leather* samples recovered from different shipwrecks around the world that were analysed in this research.

Sample Code	Location	Date	
		Wrecked	Excavation
CR1_JUKA	Juktenskobben, Finland	N/A	2017
CR2_JUKB	Juktenskobben, Finland	N/A	2017
CR3_SNi	Cape Juan de Fuca, WA, USA	1808	N/A
CR4_TEX	Texel, Netherlands	1741	2015
CR5_CAT	Plymouth, UK	1786	1972

Methods

- Destructive method - only use 1 mg
- 200 µL of solvent - $(CH_3)_2CO$:H_2O (1:1, v/v)
- 48 h soaking + 2 h sonic bath
- Centrifuge (8000 rpm) & Filter (PTFE, 0.2 µm)

Extract (200 µL)

150 µL: Dry under vacuum

50 µL: Add 350 µL 37% HCl:CH_3OH:H_2O (2:1:1 , v/v/v), 100 °C, 15 min, quench - dry under vacuum

Reconstitute in CH_3OH:H_2O (1:1, v/v), 50 µL

UPLC-PDA analysis

Compare retention times & UV-Vis spectra

Instrumentation

Ultra-high Performance Liquid Chromatography: An I-Class UPLC™ system fitted with PDA detection (210 - 800 nm) was used. The column used was a BEH C18 column (1.7 µm particle size, 50 × 2.1 mm (length × i.d.)). The elution was achieved with a gradient of MeOH in H_2O + 0.1% COOH and a run time of 10 min.

Infra-Red Spectroscopy: A FT-IR Spectrometer with diamond-ATR attachment was used for analysis of both sides of the samples: grain (outer); flesh (inner). Spectra were recorded using 24 scans with spectral resolution of 4 cm^{-1} over the absorbance range 4000 - 675 cm^{-1}.

Results

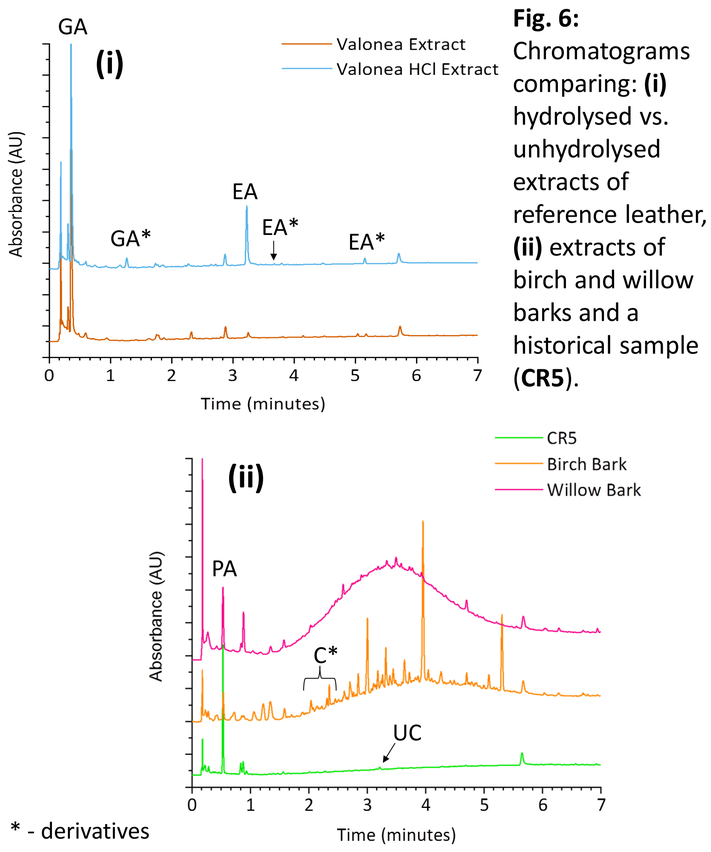


Fig. 6: Chromatograms comparing: **(i)** hydrolysed vs. unhydrolysed extracts of reference leather, **(ii)** extracts of birch and willow barks and a historical sample (**CR5**).

* - derivatives

UPLC-PDA: The increased relative absorbance's of gallic (GA) and ellagic acid (EA) (R_t = 0.308, R_t = 3.252 min, respectively) indicates the hydrolysis of *O*-glycoside bonds in hydrolysable tannins in the reference leathers. Derivatives of these compounds were also observed (**Fig. 6(i)**).

UPLC-PDA: The chromatograms for the barks and historical samples contain condensed tannins (C) and derivatives, including protocatechuic acid (PA) (R_t = 0.54 min) (**Fig. 6(ii)**). The broad peak is a non-specific indication of condensed tannins. Urolithin C (UC) (a degradation product of soluble redwood dyestuffs) was identified in the historical sample. It is known that *Russia Leather* was dyed using this source of dyestuffs.

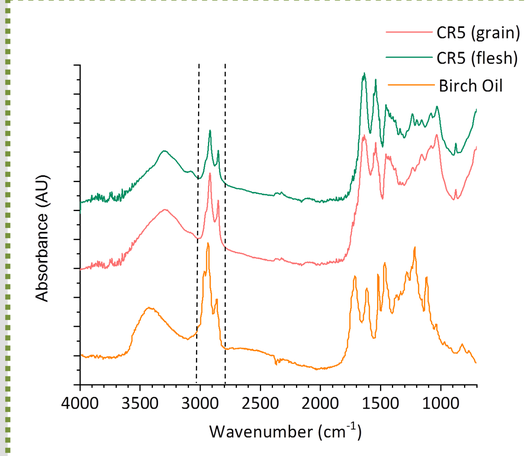


Fig. 7: FTIR spectra comparing the flesh and grain sides of **CR5** and a sample of birch oil.

Samples	Tannins		Dyes
	Condensed		UC
	PA	C	
CR5	✓	✗	✓
Birch	✓	✓	✗
Willow	✓	✗	✗

FTIR-ATR: Birch oil displayed absorbance peaks corresponding to aliphatic C-H bond stretches at 2928 & 2856 cm^{-1} (**Fig. 7**). Both the flesh and grain sides of the historical samples exhibited these peaks, with the relative intensities reflecting the degradation of the material.

Conclusion

Method Development: An improved protocol for the analysis of tannins with reduced sample size was developed.

UPLC: Characterisation of bark and historical extracts was achieved with some success, highlighting the need for further investigation.

FTIR: The extent of preservation of surface materials was determined using this technique.

Future Work

The application of mass spectrometry for analysis of historical leather should be explored. Identification and characterisation of potential markers (*e.g.* protocatechuic acid) and the construction of a reference library will be essential for the further exploration of archaeological materials involving tannins.

References

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