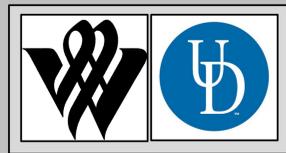
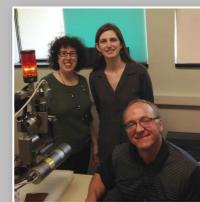


USING XRF FOR THE IDENTIFICATION OF CHROME TANNING IN LEATHER



Bruno P. Pouliot, Dr. Jennifer Mass, Lara Kaplan
Winterthur Museum and Winterthur/University of Delaware Program in Art Conservation

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I. Introduction

This poster presents the results of a comparative study using x-ray fluorescence spectroscopy (XRF) to detect the presence or confirm the absence of chromium in skins and hides prepared with the most common tanning, semi-tanning, and other processing methods used on historical leather artifacts. After compiling spectra on a set of known reference samples, the technique was used to analyze a selection of collections objects from the early 20th century. XRF proved an effective and non-invasive approach for clearly identifying chrome tanned leather in modern specimens. It also detected chromium in historical objects where chrome tanning may have been used in combination with other tanning methods.



Stacking Chrome Tanned Calfskin in a Shoe Upper Leather Tannery – Philadelphia, 1910
(Fleming, L. A. 1910. *Practical Tanning: A Handbook of Modern Processes*, Philadelphia: Henry Carey Baird & Co.)

II. History of Chrome Tanned Leather

Commercial production of chrome-tanned leather began in Philadelphia in the 1890s using ore extracted from a large chromite deposit near Baltimore. Within a decade, up to 80% of light-colored leathers manufactured in the U.S. were chrome tanned, often imitating the soft kid leathers traditionally alum tawed. By the beginning of the 20th century, chrome tanning was adopted in Germany, and soon afterwards through the rest of Europe and other parts of the world. By 1925, the process was already being used to produce most shoe leathers, and today it is used as a component, often in combination with other tanning processes, in the manufacture of over 80% of leathers worldwide.

III. Manufacture and Properties

The popularity of chrome tanning was due in part to the speed of its manufacture, taking only a day instead of weeks, as required for vegetable tanning. The process is complex and has varied since its inception, but it uses basic chromium(III) sulfate as the main tanning agent, followed by fatliquoring to provide flexibility and water resistance. It produces a durable, stretchy leather with a high collagen shrinkage temperature (up to 110°C as compared to 85°C for vegetable tanned leather) and hydrophobic nature, making it particularly resistant to water, chemicals, mold, and heat—though it is damaged by perspiration. The low percentage of tanning agent left in the skin, around 4% compared to 30% in vegetable tanning, gives a versatile leather that can be used for a wide variety of final products. Chrome tanning initially produces a lightfast pale blue leather, which can be dyed a broad range of colors, and the chrome further acts as mordant for dyes.

IV. Uses

Chrome tanning is well-suited for the production of light-colored leather, often used in the clothing industry, e.g. for gloves and shoe uppers. Because of its high heat resistance, it is also a favored material for car interiors. A less obvious but widespread use is as an initial tanning agent to prevent putrefaction of skins of freshly slaughtered animals until they can be processed. To achieve particular properties for a specific end use, freshly chrome tanned leather, referred to as “wet blue,” can be retanned using a variety of tanning or semi-tanning processes, including alum tawing, vegetable tanning, synthetic tannages, or additional chrome tanning. These retanned leathers are widely used, either full grain or suede, for shoe soles and uppers, garments, upholstery, and horse gear/apparels.



Stack of “Wet Blue” Cowhides Showing Blue Color from Chrome Tanning
Ilha Tannery, Brazil (ecplaza.com)

V. Issues With the Identification of Chromium in Tanned Leather

Standard microchemical spot testing with diphenylcarbazide tends to be unreliable for identifying chrome tanning, given the difficulties encountered separating the strongly bound chromium ions from the collagen matrix, and also because only a very small quantity of chromium is present. Identification is further complicated by the fact that many modern leathers are retanned, combining the characteristics and properties of multiple tanning processes. Other methods of identification, which rely on assessment of visual and physical characteristics indicative of chrome tanning, are subjective and prone to error.

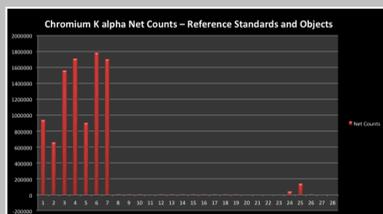
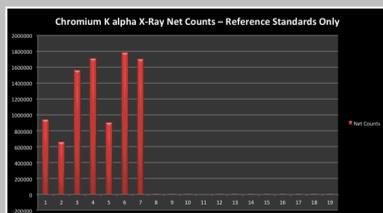
VI. Using XRF to Identify Chromium in Leather

Experimental Parameters

To test for chromium, the top and bottom surfaces (grain and flesh sides, if they could be identified) of 19 samples of modern tanned, semi-tanned, and untanned skins and hides were analyzed with x-ray fluorescence (XRF). Analysis was then performed on eight objects: two contemporary items from the Winterthur/University of Delaware Program in Art Conservation study collection, and six late 19th-early 20th century personal accessories from the Winterthur collection. Objects chosen represented a range of leather colors, from white to yellow, red, pale brown, and black; they included shoes, gloves, a purse, sewing accessory cases, and a camera case. A Bruker Artax XRF with a rhodium x-ray tube and a polycapillary focusing optic was used for all analyses. The tube was operated at 50 kV and 400 microAmps for 100 second collection times.

Comparative Results and Discussion – Chromium Levels

Chromium was consistently and readily detected on the chrome-tanned reference samples (Samples 1-7, see Spectra Group 1), while it was notably absent on rawhide and on samples processed with a range of other semi-tanning and tanning methods (Samples 8-19, see Spectra Group 2 and Graph 1). Though minor differences were found comparing the analyses of the top and bottom surfaces of the samples, the overall results remained the same, and only the data for the top surfaces are presented here. Of the eight objects tested, only two Winterthur collection objects—a pair of kid gloves and a clothespin case (Objects 24 and 25)—had chromium in large enough amount to suggest chrome tanning as part of their manufacturing process (see Spectra Group 3). These amounts were not as high as those seen in the chrome tanned reference samples (see Graph 2 and Spectra Groups 1 and 3, noting that the Y axis is the same for all groups of spectra shown). The difference could potentially be a reflection of the varying thickness or density of the leathers, particularly as both museum objects that tested positive are much thinner than all reference samples. It could also indicate changes in the chrome tanning manufacturing process since the early 20th century, or more likely be a result of the leather on these objects being first chrome tanned and then retanned with another process to provide a product with specific qualities and feel.



Graphs 1. and 2. Comparative Chromium K Alpha Counts for Reference Standards (Top) and Reference Standards and Collections Objects (Bottom)

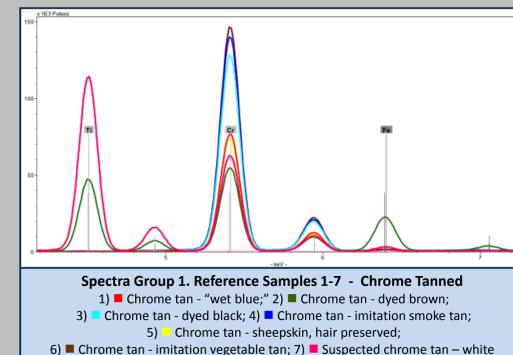
Other Relevant Findings

Other elements besides chromium were routinely detected in the reference samples, namely titanium, calcium, iron, chlorine, sulfur, and potassium. Most of these elements are expected from processes used during the pre-tanning, tanning, and finishing stages of leather manufacture, yet a few preliminary inferences may be surmised.

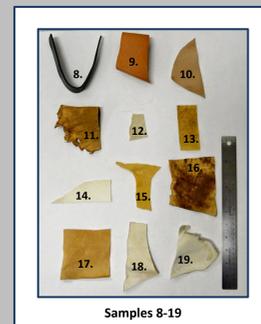
- Titanium and iron are most likely from additives and colorants used in finishing, for instance titanium to achieve a whiter color.
- Chlorine was at first believed to be from salt applied prior to tanning, yet comparing samples of salted vs unsalted brain/smoke tanned deerskin did not reveal significant differences in the levels detected. Its presence more likely indicates that a chloride salt was used as a component of the tanning process, or it could also be related to past usage.
- Aluminum was not found, even in alum tawed samples, because of the experimental conditions used (air-path analysis). Microchemical spot tests or SEM-EDS remain good options to detect this element in leather.



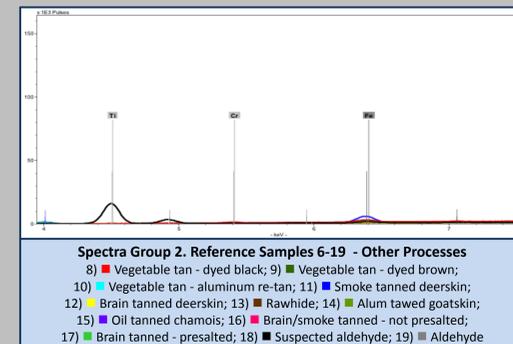
Samples 1-7



Spectra Group 1. Reference Samples 1-7 - Chrome Tanned
1) Chrome tan - “wet blue”; 2) Chrome tan - dyed brown;
3) Chrome tan - dyed black; 4) Chrome tan - imitation smoke tan;
5) Chrome tan - sheepskin, hair preserved;
6) Chrome tan - imitation vegetable tan; 7) Suspected chrome tan - white



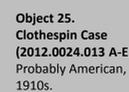
Samples 8-19



Spectra Group 2. Reference Samples 6-19 - Other Processes
8) Vegetable tan - dyed black; 9) Vegetable tan - dyed brown;
10) Vegetable tan - aluminum re-tan; 11) Smoke tanned deerskin;
12) Brain tanned deerskin; 13) Rawhide; 14) Alum tawed goatskin;
15) Oil tanned charmois; 16) Brain/smoke tanned - not presalted;
17) Brain tanned - presalted; 18) Suspected aldehyde; 19) Aldehyde

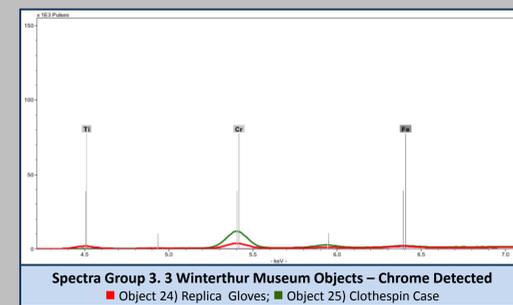


Object 24.
Gloves
(2013.0026.003 A,B)
Replica of 1790 Kid Gloves.
Paris, likely first quarter of
20th century.



Object 25.
Clothespin Case
(2012.0024.013 A-E)
Probably American,
1910s.

Images by James Schneck,
courtesy of Winterthur
Museum.



Spectra Group 3. 3 Winterthur Museum Objects – Chrome Detected
■ Object 24) Replica Gloves; ■ Object 25) Clothespin Case

VII. Conclusion

These preliminary results suggest that XRF can rapidly, effectively, and nondestructively identify chrome tanned leathers, since it can readily detect chromium ions, and lacks the dependence on binding strength that tends to make microchemical spot tests unreliable. Results are clear with modern specimens; lesser amounts of chromium detected in older leathers may be due to different thickness/density of the leathers, historical changes in tanning processes, or to retanning with other methods. The spectra also showed other elements that potentially provide useful information on how both modern and historic leather artifacts were processed.

VIII. Further Research

Further analysis of leather objects dating from the 1890s onward would confirm the effectiveness of XRF in identifying chrome tanning, as well as shed light on various factors that may affect the levels of chromium detected in the leather, such as thickness/density, changes in the chrome tanning manufacturing process, the use of combination tannages, or the possible presence of other chromium-containing compounds, for instance colorants, used in the finishing process. Investigating the efficacy of a vacuum chamber-based or helium flow XRF technique to detect aluminum would also be important, as chrome tanning was primarily used at first to imitate kid leathers traditionally produced by alum tawing. Many of the 20th century kid leather objects present in museum collections may have been produced via chrome tanning alone or in combination with alum tawing or even a pale vegetable tanning, and knowing these differences would allow these objects to be put in a clearer historical and technological context. Finally, future experiments should include the development of reference standards for quantitative XRF so that the minimum detection limits for this type of analysis can be determined.

IX. References

- Calnan, C., and B. Haines, eds. 1991. *Leather: Its Composition and Changes with Time*. Northampton, UK: The Leather Conservation Centre.
- Covington, A. D. 2009. *Tanning Chemistry. The Science of Leather*. Cambridge, UK: The Royal Society of Chemistry.
- Melich, M., Š. Palágyi, and M. Kern. 1989. Determination of Cr₂O₃ in chrome-tanned leather by radionuclide-excited X-Ray Fluorescence analysis *Isotopenpraxis Isotopes in Environmental and Health Studies* 25(8): 354-357.
- Kite, M., and R. Thomson. 2006. *Conservation of Leather and Related Materials*. Oxford: Butterworth-Heinemann.
- Stellmach, J. J. 1990. The commercial success of chrome tanning: a study and commemorative. *Journal of the American Leather Chemists Association* 85: 407-424.
- Thomson, R. S. 1997. When did chrome tanning start? *Leather Conservation News* 13(1): 1-3.