

*Antonio da Costa^{1,2}, Fernanda Correa², Gustavo Sant'Anna¹,
Sheyla de Carvalho³, Fernanda dos Santos³ and Marcia Lutterbach³*

SCANNING ELECTRON MICROSCOPIC CHARACTERIZATION OF IRON-GALL INKS FROM DIFFERENT TANNIN SOURCES – APPLICATIONS FOR CULTURAL HERITAGE

¹*Museu de Astronomia e Ciencias Afins/LAPEL*

R. General Bruce 586, S. Cristovao, Rio de Janeiro, RJ, 20921-030, Brasil; antoniocosta@mast.br

²*Universidade do Estado do Rio de Janeiro/PPG-EQ*

R. S. Francisco Xavier 524, Rio de Janeiro, RJ, 20510-450, Brasil

³*Instituto Nacional de Tecnologia/LABIO, Venezuela Ave., 82, Rio de Janeiro, RJ, 20081-312, Brasil*

Received: August 28, 2014 / Revised: September 03, 2014 / Accepted: September 30, 2014

© da Costa A., Correa F., Sant'Anna G., de Carvalho S., dos Santos F., Lutterbach M., 2014

Abstract. Scanning electron microscopy was used to study the reactivity of iron-gall inks with varying iron concentrations. Vegetable extracts with hydrolysable tannins produced stable ink, while the presence of crystal aggregates explained the low reactivity of condensed tannins. This novel archaeometric approach has proved useful in chemical corrosion studies of ancient documents.

Keywords: iron-gall ink, corrosion, tannin quantification, cultural heritage, scanning electron microscopy.

1. Introduction

Iron-gall inks were very common between 12th and 19th centuries all over the world and particularly in South America until the 20th century [1-2]. The classical formula for an iron-gall ink includes four basic ingredients: vegetable galls (mostly Japanese and Chinese galls, British and American oak galls and Aleppo galls), ferrous sulfate, gum arabic and an aqueous medium such as wine, vinegar, beer, urine, etc. Tannic acid present in distinct oaks reacts with iron from ferrous sulfate, resulting in a soluble complex known as ferrous galotanate. Due to its solubility, the ink easily penetrates the surface of the paper. Upon exposure to high oxygen concentrations for a specified time period, a dark insoluble pigment is formed, which is not easily removable or degraded [3-6].

Iron-gall ink becomes stable when prepared at a specific stoichiometric ratio of tannic acid vs. ferrous sulfate [7]. However, most iron-gall inks found in ancient manuscripts present an excess amount of iron, thus

contributing to cellulose degradation due to the action of the iron-gall ink. Excess iron present in the ink can contribute to the degradation of manuscripts through two basic mechanisms: the first mechanism is acid-catalyzed hydrolysis, where the degradation of cellulose is accelerated by the presence of sulfuric acid produced during the formation of the complex in iron-gall ink [8]; while the second mechanism is one in which soluble ferrous ions catalyze oxidation reactions in two distinct processes: in the first, ferrous ions contribute to the breakdown of cellulosic chains, releasing organic radicals and peroxides, which are both highly reactive, thus resulting in a decrease in the amount of cellulose polymers. The highly reactive hydroxyl radical is formed by the action of iron; this radical easily extracts hydrogen ions from any other molecule, contributing to chain reactions with cellulose [9] (Fig. 1).

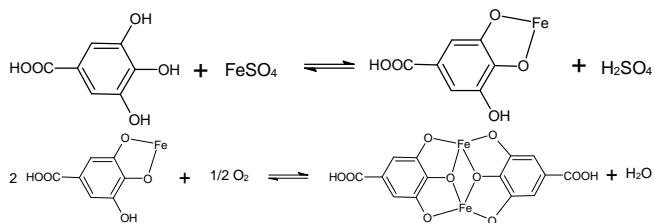


Fig. 1. Reaction mechanism of tannin oxidation in the presence of ferrous sulphate

Excess oxidation in iron-gall inks in old recipes is not only attributed to the presence of iron but also to the source of tannin used. Vegetable tannins are natural

polyphenolic compounds with a broad structural composition found in 30 % of higher plants [10-13].

Tannin concentration changes according to the type of vegetable tissue, age of the plant, and the region where the plant is typically found [14]. According to their chemical structure, tannic compounds can be classified into two types: hydrolysable and condensed ones. Hydrolysable tannins are composed of a mixture of simple phenols such as ellagic, pirogallol, gallic, and digallic acid esters with sugars such as glucose. Gallotanic acid, the chemical species responsible for the complexation reaction with iron, is produced from the hydrolysis of hydrolysable tannins. Thus, the complex formed in the iron-gall ink could easily be obtained with hydrolysable vegetable tannins [7, 15-16]. In contrast, condensed tannins are flavonoid units with different degrees of condensation and are composed of flavan-3-ols (catechin) or flavan 3,4-diols (leucoanthocyanins). These substances are highly resistant to hydrolysis, explaining their non-reactive nature with iron [10, 17]. However, several historical documents written with iron-gall inks used old recipes based on the use of condensed vegetable tannins, thus explaining why iron ions are easily released. Consequently, corrosion of the paper is accelerated by excess iron associated with only a small amount of reactive tannins.

In addition to this accelerated oxidation due to the natural aging of iron-gall inks, formation of crystals on surface paper fibers can be observed due to excess inorganic salt [18]. A great number of manuscripts clearly show the presence of crystal or amorphous deposits on their surfaces, particularly those with a high content of ink [19, 20]. The sediments usually found in documents containing iron-gall inks are calcium, potassium and iron oxalates, calcium sulfate, calcium carbonate and ferrous sulfate [20]. The process of crystallization is usually characterized by optical microscopy, and, in some cases, is clearly macroscopically observed.

Based on these descriptions, the objective of the present paper is to use scanning electron microscopy to observe aggregates on the surface of paper fibers where iron-gall inks were deposited, with different iron/tannin ratios, accelerated thermal aging, and different tannin sources. These observations were correlated with oxidation levels and tannin types.

2. Experimental

2.1. Iron-Gall Inks

Iron-gall inks were prepared with $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (Vetec, Brazil), tannic acid (Acid) ($\text{C}_{76}\text{H}_{52}\text{O}_{46}$) (Vetec, Brazil) or, alternatively, vegetable tannins were obtained from *Castanea sativa* (Chestnut), *Caesalpinia spinosa* (Pod) and *Acacia* sp. (Liana), both supplied by TANAC

(Brasil). Other ingredients also included gum arabic (Vetec, Brazil) and ethanol (Vetec, Brazil). Inks were prepared according to Table 1.

*Table 1
Synthetic iron-gall inks used in the experiments*

Ink group	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, g	Tannic acid or vegetable tannin, g	Gum Arabic, g	Ethanol, ml
1	1	5.5	2.0	5.0
2	2	5.5	2.0	5.0
3	10	5.5	2.0	5.0

Iron-gall inks were prepared at room temperature and pressure, exposed to atmospheric air for 24 h to help both fixation of the components on Whatman paper strips and the formation of the gallotanic complex. After that step, paper strips were kept in sealed vessels protected against light.

Paper strips (6.0x1.0 cm) were immersed for 5 min in vertical flasks containing the inks, dried at room temperature for 2 h and placed in a closed chamber at 373 K for 5 days, according to the procedure adopted by International Standard Organization to accelerate aging and oxidation.

2.2. Scanning Electron Microscopy

The morphology of ink aggregates on the surface of paper strips was observed by Scanning electron microscope (Inspect, S 50 FEI). Several images were taken in areas distributed for each sample, and the figures in this paper show representative areas for each sample, as they were morphologically homogeneous. Samples were prepared by coating with gold target in sputtering equipment EMITECH K550X for 3 min at 20 mA. The images were observed under high vacuum mode with a 20 kV voltage and 400x magnification for complete characterization.

2.3. Crude Tannin Extracts from Vegetable Tannins

Crude tannin extracts were obtained from the commercial tannin samples supplied according to the procedure suggested by S. George *et al.* [21]. To obtain the extracts, vegetable tannins (0.1 g) were added to ketone solution (20 ml, 70 % v/v) in Erlenmeyer flasks. Those flasks were shaken in a rotary shaker (Tecnal, Brazil) at 150 rpm for 20 min at room temperature. After that period, solutions containing the extract were filtered using Whatman filter paper and supernatant solutions were used for the determination of total and condensed tannins in the original samples.

2.4. Total Tannins

Initially, according to the procedure suggested by S. George *et al.* [21], total phenolic compounds were

quantified by using a crude extract (0.5 ml) obtained previously, and adding the Folin-Ciocalteau reagent (2.5 ml, 10 % v/v). After that, the sample was agitated at room temperature for 2 min, and sodium carbonate solution (2.0 ml, 7.5 % v/v) was added. Previously mixed solutions were placed in a water bath at 323 K for 15 min. After this procedure, tubes were cooled and spectrophotometric determinations were performed at 760 nm (Varian Specord, Brasil).

To precipitate the tannins, the extracts (5.0 ml) were diluted in water (10 ml) and precipitated with casein (1.0 g), under constant agitation at room temperature for 3 h, according to the methodology proposed by R. Silva *et al.* [22]. After that, similar to a previously used procedure, solutions were filtered and the filtrate was used for the quantification of residual phenolic compounds. The amount of total tannins corresponds to the difference between the concentration presently found and the total concentration of phenolic compounds. The standard sample used in this method was tannic acid and the results were expressed as mg of equivalent tannic acid/g sample.

2.5. Condensed Tannins

The concentration of condensed tannins in the commercial samples was determined according to the methodology proposed by M. Machado [23]. Crude extract (0.1 ml) and methanol (0.9 ml) were added to laboratory tubes, followed by the addition of a methanol-acid solution (2.5 ml, 8.0 ml of hydrochloric acid in 100 ml of methanol) and a vanillin solution (2.5 ml, 1.0 g of vanillin in 100 ml of methanol). The samples thus prepared were heated in a water bath at 333 K for 10 min and spectrophotometric determinations were performed at 525 nm (Varian Specord, Brasil). The standard sample used in this method was pyrogallic acid and the results were expressed as mg of pyrogallic acid equivalents/g sample.

3. Results and Discussion

3.1. Iron-Gall Inks

Macroscopically, no substantial differences were found in viscosity, homogeneity, and color intensity in the different inks prepared according to the methodology. In fact, the stoichiometric ratio for the production of a stable ink has been known since the 17th century. However, it is also known that among European recipes from the 15th to the 19th centuries there was 50 % increase in the number of distinct recipes, which usually differed based on the their excess iron content.

In the present research, accelerated thermal aging of the ink impregnated paper strips showed gradual changes in color intensity and aspect. All the prepared samples, in each of the tannin/ferrous sulfate ratios, clearly presented signs of oxidative processes. However,

these oxidations were markedly different in each preparation. Inks prepared with the pod tannin presented a very low degree of oxidation, with a decreased discoloration, that was particularly present in the borders of the ink in the paper strips. It can be clearly noted that the oxidation tends to increase from ink 1 to 3, thus confirming that excess iron in a sample contributes to corrosive action. Similar behavior was observed when tannins chestnut and acid samples were used.

On the other hand, inks prepared with the use of Liana tannin presented a distinctly different behavior in comparison to the above mentioned tannin samples. Oxidation of the ink-impregnated strips occurred not only in the borders of the paper but also in the entire area of the strips. This behavior seemed initially confusing, as the amount of Liana tannin used was the same as the amount used for the remaining tannin samples. Thus, it seemed that the reaction of iron with Liana tannin was decreased in comparison to the others.

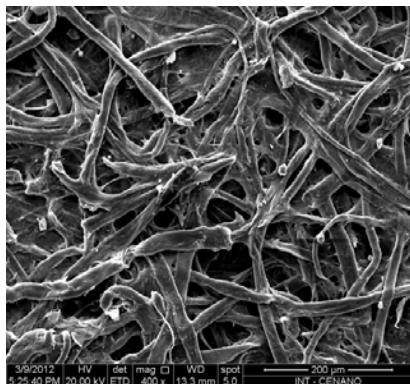
B. Reissland [24] observed degradation caused by iron-gall inks in test paper strips prepared with 5.5:1.0 iron:tannin ratio. Accordingly, paper strips were artificially aged at 363 K for up to 18 days and observed under visible and ultraviolet light. B. Reissland used this technique to detect the gradual degradation of the paper strips due to the presence of oxidized ink. He observed that after three days, a green fluorescence was observed in the area containing the ink, followed by a stronger color after six days. After that, the fluorescence became pale, gradually turning to yellow, followed by complete discoloration. This final stage of discoloration was followed by a complete loss of mechanical strength of the paper, indicating the deleterious effect of the oxidized ink on cellulose fibers.

3.2. Scanning Electron Microscopy

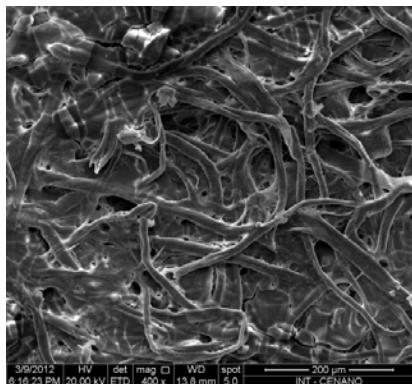
According to M. Hey [25], low electron acceleration voltages, such as 5 to 10 kV contribute to a better definition of images captured at the surface of papers. In the present work 20 kV voltage was used because it was our purpose to observe crystal depositions on the surface of the fibers and not to delineate crystal morphological aspects.



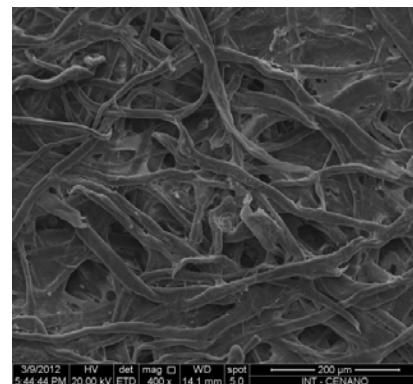
Fig. 2. SEM of a Whatman white paper strip not impregnated with iron-gall ink (magnification of 400x) – blank



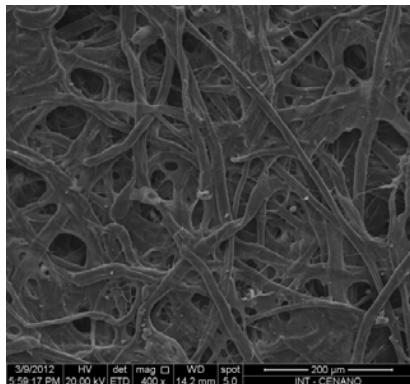
a)



b)

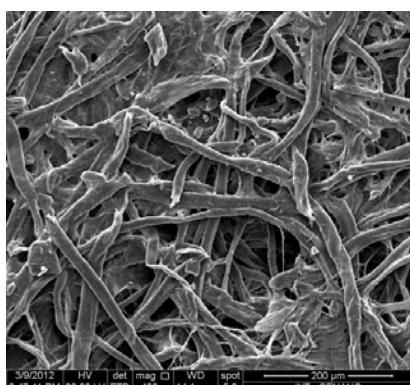


c)

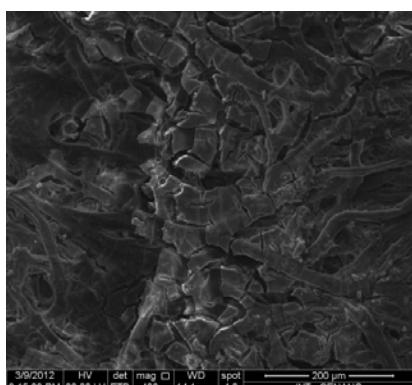


d)

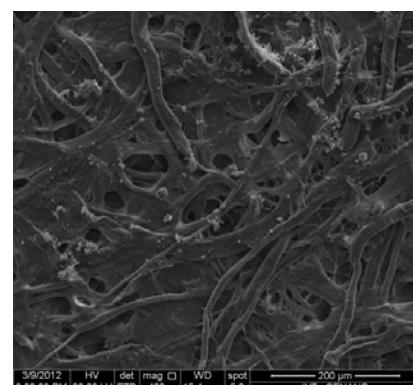
Fig. 3. SEM of iron-gall-ink-impregnated paper strips (magnification of 400x). Tannins: cid (a); liana (b); chestnut (c) and pod (d); Group 1 ink, iron:tannin ratio – 1:5.5



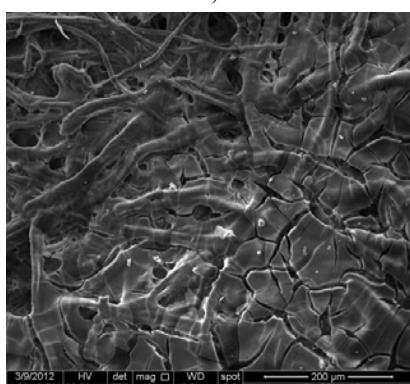
a)



b)



c)



d)

Fig. 4. SEM of iron-gall ink impregnated paper strips (magnification of 400x). Tannins: acid (a); liana (b); chestnut (c) and pod (d); Group 2 ink, iron:tannin ratio – 2:5.5

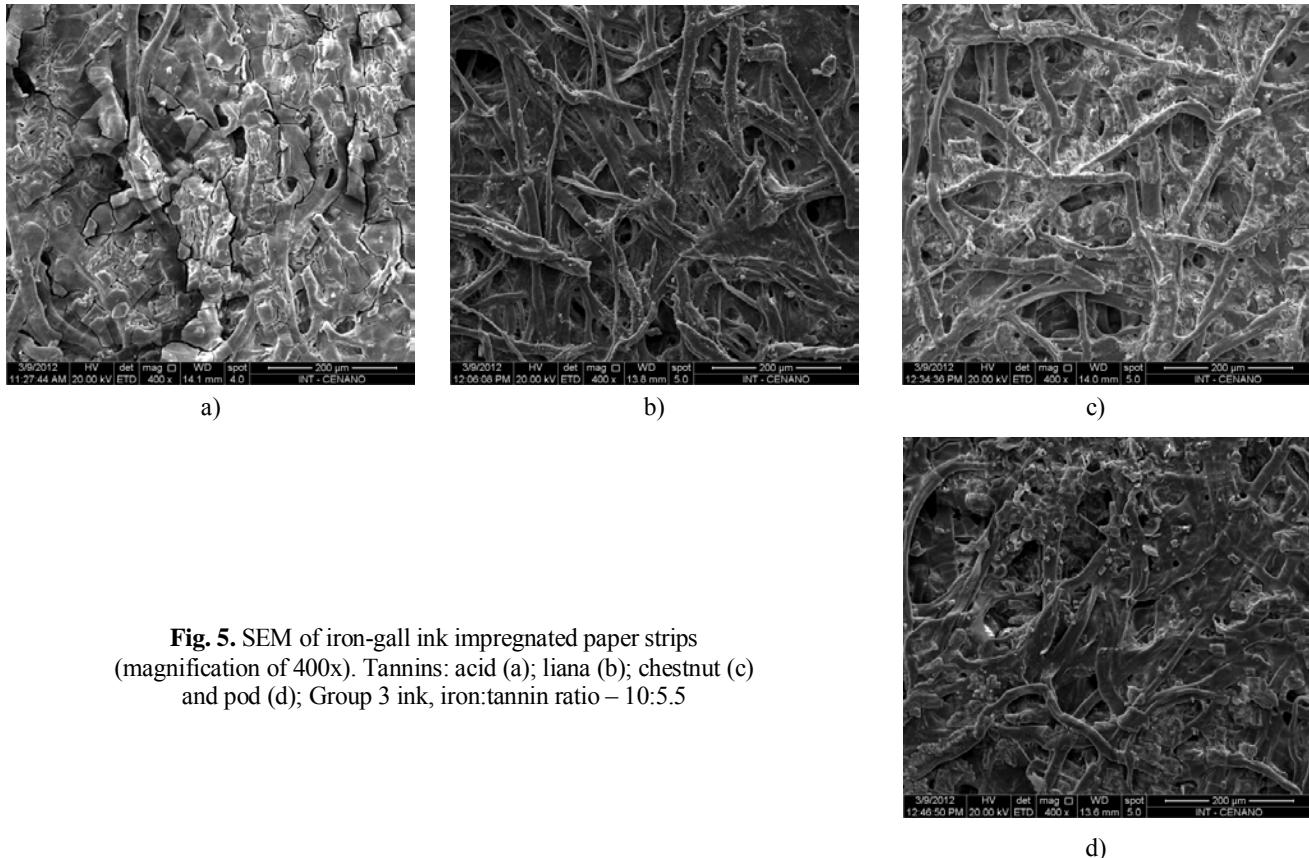


Fig. 5. SEM of iron-gall ink impregnated paper strips (magnification of 400x). Tannins: acid (a); liana (b); chestnut (c) and pod (d); Group 3 ink, iron:tannin ratio – 10:5.5

Fig. 2 shows cellulose fibers of a Whatman paper strip not impregnated with iron-gall ink (Blank). Long fibers, typically arranged in a non-regular surface, can be observed in the paper strip, in addition to the presence of empty spaces and lack of any deposited matter among the fibers. According to M. Conceicao *et al.* [26], typical cellulose fibers present high amounts of calcium carbonate.

According to M. Anguera [27] and D. Camera [18], the occurrence of crystal particles in drawings and documents impregnated with iron-gall ink, can be seen on pieces where the ink was added in high amounts. By capillary action the ink is gradually absorbed through the fibers, staying on the surface of the paper as small chemical deposits.

After just a few days, it was possible to observe marked differences in the paper strips impregnated with iron-gall ink at different iron:tannin ratio, particularly in reference to the commercial tannin source used in the preparation. Fig. 3 shows SEM images of Group 1 iron-gall inks with three different tannin sources. From the images, a close similarity between the iron-gall ink impregnated strips and the control sample can be seen. The SEM image of the acid sample shows that some empty spaces of the cellulose fibers were filled with ink, with a rough film and small crystal particles. D. Camera [18] working with iron-gall inks, prepared in laboratory and with considerable amount of tannin, proved that a

uniform ink film is formed on the surface of the paper, even without the introduction of agglutination compounds. According to A. da Costa *et al.* [7], commercial tannic acid is a mixture of gallotannins produced in different parts of vegetables. Due to this nature, it is possible that a small amount of iron present in the ink becomes amenable to oxidation, which is corroborated by the presence of small crystal particles under SEM. It is also known that chestnut and pod tannins exhibit variable composition and amount of tannins. This can be a possible explanation for the similarities between SEM images among commercial vegetable sources and the acid sample.

Differences amongst images from Fig. 3, in comparison to the blank in Fig. 2, are due to a continuous dense film on the empty spaces, as well as some cellulose fibers completely covered with the same film. According to A. da Costa *et al.* [7] liana tannin is a type of condensed tannin with very low reactivity to metal ions. Due to this nature, condensed tannins are unable to form complex molecules with iron ions. Thus, in comparison to the other tannin sources previously tested, there is a low content of hydrolysable tannins available to react with iron. Most likely, insoluble oxide crystals were formed during oxidation of iron, due to the lack of available tannic molecules to

react with iron. Consequently, the formation of crystal deposits in the cellulosic fibers is expected, and this formation was confirmed by the SEM images.

Iron-gall inks from Group 2 were prepared with 2 g of ferrous sulphate in the formulation (Fig. 4). In comparison to the blank test, small deposits can be observed among the fibers. Theoretically, inks prepared with acid sample present a higher reactivity with iron, in comparison to other tannic substances. Thus, it is expected to have smaller formation of deposits among the fibers when the acid sample is tested.

Formation of deposits on the surface of the paper strips in the cellulosic fibers of the paper is clearly observed. The lack of empty spaces among the fibers can be observed as a continuous film, clearly rougher than the ones previously observed. This behavior, in comparison to the acid sample, can be explained by the nature of the tannins present in the commercial vegetable formulations, where a natural variability in concentration is expected. This is an indication that the amount of tannin added during the formulation of the inks, although theoretically correct, is not directly related to their reactivity, because purity and content need to be confirmed. Consequently, when paper strips were impregnated with iron-gall inks, the amenability of the inks to oxidation could not be predicted, due to the undefined concentration of reactive tannins in commercial samples.

To confirm this assumption, Fig. 5 presents SEM images of Group 3 iron-gall inks (iron concentration was ten times higher than the ones from Group 1). Again, inks prepared with the acid sample presented the highest reactivity between iron and tannins, confirmed by the lack of aggregates among the fibers, in comparison to inks prepared with commercial vegetable tannins. Surprisingly, a much higher formation of aggregate deposits on the surface of paper strips was expected compared to Group 1 inks. Inks prepared with commercial vegetable sources showed a marked presence of aggregate deposits among the fibers.

3.3. Total Tannins Quantification

To determine the total amount of tannin in the samples, tannic acid was used as the standard substance. Its high content of hydrolysable tannins is widely recognized in the literature [12]. Table 2 presents the total tannin concentrations in the vegetable extracts used in the present work.

No marked differences were detected in the total content of tannins in both vegetable extracts, although the pod sample presented a decreased content. According to P. Krisper et al. [28], tannins from *Castanea* plants are produced in different parts of the world and are easily extracted with hot water. Tannin content in the plant

depends on the age of the plant and particular tissues of the plant. The authors also informed that plants from 15 to 71 years present total tannin content ranging from 6.9 to 10.7 %. They also concluded that surface, intermediate and inner layers of the plant present variable tannin contents. In another study, C. Mao et al. [29], proved that in the *Castanea mollissima* species, the total content of tannins ranged from 2.41 to 5.13 %, depending on the extraction technique used. These results seem to agree with the present quantification.

Table 2

Total tannin concentration in vegetable extracts

Source	Total tannin content, % equivalent tannic acid
<i>Castanea sativa</i> (chestnut)	4.62 ± 0.11
<i>Caesalpinia spinosa</i> (pod)	3.00 ± 0.53
<i>Acacia</i> sp. (liana)	4.62 ± 0.51

In relation to *Caesalpinia* species, C. Siqueira et al. [30] investigated the levels of tannins and flavonoid compounds in medicinal plants, using extraction with 50 % (v/v) methanol solution. Among dozens of species studied, *Caesalpinia pyramidalis* presented one of the highest amounts of total tannins, approximately 6.01 %.

In the work of A. Aganga et al. [31] total tannin concentration in the leaves and strips of the plant ranged from 0.5 to 11.2 %, depending on the species and tissue (Table 3). The sample liana tannin used in the present work is a mixture of several *Acacia* species. Thus, a direct comparison between our results and the results from Ref. [31] should not be done. If we instead consider average values, a value of 3.8 % is found, which is close to the value calculated in the present work.

Table 3

Total tannin content in *Acacia* species [31]

Species	Total tannins, %
<i>Acacia burkei</i>	0.8
<i>Acacia erubescens</i>	1.9
<i>Acacia fleckii</i>	1.3
<i>Acacia galpanii</i>	11.2
<i>Acacia giraffae</i>	0.5
<i>Acacia kirkii</i>	6.5
<i>Acacia mellifera</i>	0.9
<i>Acacia robusta</i>	8.0
Average value	3.8

M. Pansera et al. [12] extracted tannins from *Acacia mearnsii* species using supercritical fluids. High concentrations of total tannins were obtained. However, when methanol, ethanol, and water were used as solvents

in the supercritical extractions, total tannin concentration ranged from 4.0 to 9.0 %, depending on the solvent used.

In another work, K. Rana *et al.* [32] found higher total tannin concentrations in the *Acacia nilotica* species. Authors attributed this high content to seasonal variations and the method used for extraction (70 % (v/v) ketone solution and Folin-Ciocalteau reagent, using tannic acid as primary standard). The total average content in the plant was equal to 14.6 %.

As seen from the literature, there is a wide variability among the results, depending on the plant species, method of extraction and procedure for quantification. It can thus be concluded that quantification of the total tannins concentration cannot be the only procedure to corroborate SEM observations. Thus, the values obtained in this study cannot be used to confirm the oxidative behavior observed on the paper strips through SEM. This is particularly true if the liana tannin is considered. Consequently, the investigation of condensed tannins content in the samples can elucidate this phenomenon.

3.4. Condensed Tannins Quantification

The total condensed tannins quantification is highly complex, due to the diversity of chemical structures found in this group of compounds. Sample collection, drying process and extraction methods markedly affect the quantification of these compounds. These limitations contribute to some drawbacks in the determination of high molecular weight substances and insoluble compounds. Vanillin is highly used due to its reactivity with condensed tannins [33].

According to P. Schofield [33] the choice for a suitable standard substance to compare the results is the critical point in the determination of the total condensed tannins in a vegetable sample. In fact, an internal standard, directly extracted and purified from the material to be quantified is the best standard to be chosen. However, it is not always possible to perform this extraction. Thus, according to the literature, pyrogallic acid can be used as a reliable standard. Results of condensed tannins content in vegetable extracts are presented in Table 4. From these results, it is clear that the selected method did not detect the presence of condensed tannins in chestnut and pod vegetable extracts. This is in close agreement with SEM results, which showed decreased detection of aggregate particles on the surface of the paper strips, confirming that condensed tannins are most likely absent in those samples, thus contributing to the reactivity of iron-gall inks. The higher content of condensed tannins in the liana sample also corroborates the SEM images: the high amount of aggregates on the paper strips impregnated with iron-gall inks can be related to the amount of condensed tannins,

explaining the low reactivity of *Acacia* tannins with the iron added to the inks.

Table 4

Condensed tannins quantification in commercial vegetable samples

Source	Total tannin content, % equivalent pyrogallic acid
<i>Castanea sativa</i> (chestnut)	N. D.
<i>Caesalpinia spinosa</i> (pod)	N. D.
<i>Acacia</i> sp. (liana)	60.0 ± 2.5

Note: N.D. – not detected

J. Zivkovic *et al.* [34] extracted condensed tannins from the *Castanea sativa* species with 50 % (v/v) ethanol solution, followed by filtration and quantification by the vanillin method. Average values indicated the presence of small amounts of condensed tannins, from 1.02 to 2.62 %. M. Kardel *et al.* [35] studied four different vegetable extracts, using 70 % (v/v) ketone and determining the total condensed tannins content through the butanol method. The authors also found a low concentration of condensed tannins (0.46 %) in *Caesalpinia spinosa*, corroborating the results from the present work.

The high content of aggregates in the cellulose fibers found in the Liana vegetable extract, in comparison to the remaining extracts, is corroborated by the high amount of condensed tannins found here, approximately 60 %. J. Carulla *et al.* [36] working with the same liana tannin used in the present work found a total condensed tannins content equal to 61.5 %, consistent with the results from the current work. C. Grainger *et al.* [37] also quantified the total content of condensed tannins from *Acacia mearnsii* and found 60.3 % content, using the methodology proposed by J. Carulla *et al.* [36].

4. Conclusions

Depending on the tannin source used in the preparation of iron-gall inks, iron oxidation levels were markedly different. This oxidation is partially explained by the formation of dense aggregate particles on the surface of paper strips.

Scanning electron microscopy proved to be a useful tool for the investigation of stages of iron-gall ink degradation on the surface of paper through the identification of crystal particles and aggregates, confirming the lack of reactivity between iron and tannins from different recipes.

Increasing iron concentrations in the different ink preparations can be related to oxidation through scanning electron microscopy analysis and the nature of the tannin,

hydrolysable or condensed, is a clear indication that degradation patterns can be explained in terms of reactivity.

Iron-gall inks prepared with tannic acid and hydrolysable tannin sources from *Castanea sativa* and *Caesalpinia spinosa* are more stable due to higher reactivity with iron. Condensed *Acacia* sp. tannins present lower reactivity with iron, thus contributing to the formation of aggregates on the surface of paper strips, a fact that can be confirmed by scanning electron microscopy.

Total tannins concentration did not explain the observed reactivity patterns in iron-gall inks. However, the determination of condensed tannins did explain the formation of aggregate particles in microscopic observations. This technique, in association with scanning electron microscopy, presents an insight into the use of archaeometric techniques for the preservation of cultural heritage.

References

- [1] Albro S. and Biggs J.: Library of Congress Inform. Bull., 2008, **67**, 115.
- [2] Leal J.: Tintas para escrever, Documento Monumento, 2010, **2**.
- [3] Cleveland R.: The Iron Gall Ink Meeting. University of Northumbria, Newcastle Upon Tyne, September 2000, 23.
- [4] James C.: *ibid*, 13.
- [5] Hahn O.: Restaurator, 2010, **31**, 415.
- [6] Hahn O. and Wolf T.: [in:] Renn J., Schlogl R. and Schutz B. (Eds.), The Equilibrium Controversy, Sources 2, Edition Open Access 2012, 271.
- [7] da Costa A., Fonseca N., Carvalho S. et al.: Central Eur. J. Chem., 2013, **11**, 1729.
- [8] Krekel C.: Int. J. Forensic Doc. Exam., 1999, **5**, 54.
- [9] Maitland C.: AIC 37th Annual Meeting. Los Angeles, California 2009, 37.
- [10] Haslam E.: Plant Polyphenols – Vegetable Tannins Revisite. Cambridge University Press, Cambridge 1989.
- [11] Zucker W.: The American Naturalist, 1983, **121**, 335.
- [12] Pansera M., Santos A., Paese K. et al.: Revista Brasileira de Farmacologia, 2003, **13**, 17.
- [13] Haroun M., Khirstova P. and Covington T.: J. Forest Products & Industries, 2013, **2**, 21.
- [14] Monteiro J., Albuquerque U., Araujo E. et al.: Quimica Nova, 2005, **28**, 892.
- [15] Battestin V., Matsuda L. and Macedo G.: Alimentos e Nutricao, 2004, **15**, 63.
- [16] Hergert H.: Adhesives from Renewable Res., 1989, **385**, 155.
- [17] Trugillho R., Caixeta R., Lima J. et al.: Cerne, 1997, **3**, 1.
- [18] Camera D.: AIC 32nd Annual Meeting. USA Oregon, Portland 2004, 75.
- [19] Ferrer N. and Sistach M.: Restaurator, 2005, **26**, 105.
- [20] Ferrer N. and Sistach M.: Restaurator, 2013, **34**, 175.
- [21] George S., Brat P., Alter P. et al.: J. Agricult. & Food Chem., 2005, **53**, 1370.
- [22] Silva R., Akisue G., Coelho M. et al.: 4th Int. Congr. on University–Industry Cooperation. Brazil, Taubate 2012.
- [23] Machado M.: M.Sc. thesis, Universidade Federal de Santa Maria, Brazil 2007.
- [24] Reissland B.: The Iron Gall Ink Meeting. University of Northumbria, Newcastle Upon Tyne, September 2000, 109.
- [25] Hey M.: Restaurator, 1970, **1**, 233.
- [26] Conceicao M., Ferreira G. and Ribeiro R.: XX Jornada de Iniciacao Cientifica, CETEM, Brasil 2012.
- [27] Anguera M.: Restaurator, 1996, **17**, 117.
- [28] Krisper P., Tisler V., Skubic V. et al.: [in:] R. Hemingway and P. Laks (Eds.), Plant Polyphenols. Plenum Press, New York 1992.
- [29] Mao C., Zhao S., Liu J. Y. et al.: Molecules, 2011, **16**, 1.
- [30] Siqueira C., Cabral D., Sobrinho T. et al.: Levels of Tannins and Flavonoids in Medicinal Plants: Evaluating Bioprospecting Strategies, Evidence-Based Complementary and Alternative Medicine, vol. 9, 2012.
- [31] Aganga A., Tsopito C. and Morake K.: XVIII Int. Grassland Congr., Winnipeg, Manitoba 1997.
- [32] Rana K., Wadhwa M. and Bakshi M.: Asian-Australasian J. Animal Sci., 2006, **19**, 1134.
- [33] Schofield P., Mbugua D. and Pell A.: Animal Feed Sci. Techn., 2001, **91**, 21.
- [34] Zivkovic J., Mujic I., Zekovic Z. et al.: J. Central Eur. Agricult., 2009, **10**, 3.
- [35] Kardel M., Taube F., Schulz H. et al.: J. Appl. Botany and Food Quality, 2013, **86**, 154.
- [36] Carulla J., Kreuzer M., Machmuller A. et al.: Australian J. Agricul. Res., 2005, **56**, 961.
- [37] Grainger C., Clarke T., Auldist M. J. et al.: Canadian J. Animal Sci., 2009, **89**, 241.

СКАНУЮЧО-ЕЛЕКТРОННОМІКРОСКОПІЧНІ ХАРАКТЕРИСТИКИ ГАЛЛ-ЗАЛІЗНИХ ЧОРНИЛ З РІЗНИХ ДЖЕРЕЛ ТАНІНУ – ЗАСТОСУВАНЯ ДЛЯ КУЛЬТУРНОЇ СПАДИШНИ

Анотація. З використанням скануючої електронної мікроскопії вивчено реакційну здатність галл-залізного чорнила з різними концентраціями заліза. Показано, що рослинні екстракти із здатним до гідролізу таніном використовують для одержання стійких чорнил, тоді як присутність кристалічних агрегатів пояснює низьку реакційну здатність конденсованих танінів. Запропоновано використовувати такий підхід для дослідження хімічної корозії старовинних документів.

Ключові слова: галл-залізні чорнила, корозія, квантифікація таніну, культурна спадщина, скануюча електронна мікроскопія.