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A Timeline of Analytical Techniques for Characterization and Treatment of Iron-gall Ink – A Brief Overview of the Last Two Decades

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Abstract

An extensive review of the published literature about the iron-gall inks was done based on searches in the main scientific publications dealing with cultural and historical heritage, chemistry, physics and paper conservation. What could be observed from this search, performed for the last two decades, is that this field faced high and low movements that contributed for the present stage of development in the preservation of documents containing iron gall inks. The search performed was divided into five distinct periods: the start of the development of studies of iron gall ink documents; the search for non-destructive techniques to understand the chemical composition of the ink; the improvement of analytical instrumental analysis; the consolidation of international groups dealing with the matter of paper conservation; and, finally, the worry and drawbacks for a practical application of the accumulated scientific knowledge. Some final considerations about interdisciplinarity in the field are also presented.

Keywords: Iron gall ink; Characterization; Treatment; Stabilization; Analytical detection.

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1. Introduction

Paper has been the most important support for historic and cultural information of mankind through centuries. In the beginning, the cellulose fibers of paper were obtained from hemp and cloth linen. The sizing process was composed of animal glue, and during the manufacture of paper, cellulose fibers easily accumulated metal ions from the aqueous process from machine papers, producing a material more difficult to fix the ink. From the 19th. Century, additives such as gelatin and alumen ($Al_2(SO_4)_3.18H_2O$) started to be added to produce a paper more suitable to writing, not only to improve the quality and resistance of the paper but also to protect it from microbiological action. At the end of 19$^{th.}$ Century the increase of the paper demand and the scarce availability of cellulose fibers from cotton and linen, increased the use of wood for this purpose; consequently, cellulose, hemicellulose and lignin (from wood pulp) became the main components of the paper. Gelatin was slowly replaced by other types of resins, mainly alumen, and more recently this additive has been added to other synthetic products such as carboxymethilcellulose [1,2]. Thus, it is evident that the evolution in paper manufacture through centuries led to a modification in paper structure, due to the source of cellulose fibers and also in relation to the additives added, although production principles are still the same [2].

From 15$^{th.}$ Century to the first decades of 19$^{th.}$ Century iron gall inks were largely used by western civilization being considered one of the most important inks in history. Many museums and galleries around the world still have large and valuable collections of manuscripts and drawings produced with iron gall inks by artists such as Leonardo da Vinci, Rembrandt van Rijn, Giovanni Francesco Barbieri, for example [3,4].

Basically, iron gall inks have four main ingredients: gallic acid, ferrous sulphate, gum Arabic and water. Gallic acid is extracted from gall nuts that contain gallotannins and the ferrous sulphate is extracted from minerals that contain many others metals as constituents, for example, copper, aluminum, magnesium and zinc sulphates. The Arabic gum is extracted from trees of the genus *Acacia*, being soluble in water and the main responsible agent for the flow and ink fixation. The mixture of gallic acid and ferrous sulphate led to the formation of ferrous gallothanate complex. This molecule is more soluble in water easily penetrating in the paper through cellulose fibers, being more difficulty to remove. In contact with oxygen, this oxidation process produces an insoluble dye of ferric gallothanate, which is more difficult to remove, contributing to its efficiency as writing ink. In order to retain these insoluble molecules in suspension in the ink, gum Arabic must be added to the moisture as thickener. Although iron gall ink is basically made of these four ingredients, it presents a large variety of recipes along the history. Furthermore, this ink can be made by natural ingredients resulting in the presence of many impurities in the different formulations. This can lead to degradation and corrosion, darkening and loss of mechanical properties of the paper in a process called *iron gal ink corrosion*.

The objective of the present paper is to provide information about analytical techniques and procedures developed in the last 20 years, trying to identify the main techniques or relevant information for every four-year period. The main sources of information were the most relevant scientific journals publishing papers in the last years, in the field of cultural heritage and applied chemistry and physics.

1.1. 1996-1999 – The void in the study of iron-gall inks

One of the main contributions of the paper of Lucarelli and Mandò was the elucidation of ink composition of several manuscripts, produced in central Italy from the 12th. to the 15th. Centuries [5]. Within the group of manuscripts the authors evaluated, a substantial difference was detected between those of the 12th. Century and all the others, possibly showing a technical evolution in the ink-making procedures. This is important as the possibility of understanding the mode of producing the ink from time to time, with a view to improve its composition and stability. Information was obtained by PIXE techniques, bringing knowledge that still today remains in the same level of investigation. From 1997 until 1999 no scientific publications were found, indicating the need for further investigations.

1.2. 2000-2003 – Non-destructive tests started to be implemented for elucidation of iron-gall inks composition

In 2000, Feber and his colleagues published a paper presenting the results of the effect of different ink compositions, mainly due to the presence of iron, tannic acid and gum Arabic, on sulphite paper [6]. Authors tested accelerated aging and concluded that the three components of the ink markedly affected the corrosive action of iron-gall inks. However, authors concluded that iron sulphate is the dominating agent, while the presence of gum Arabic and tannic acid tended to prevent oxidation.

In a paper written by Remaizelles and his colleagues PIXE technique was used, but to a different extent. The purpose of the authors was to evaluate the migration of elements such as sulphur, iron and calcium from the ink to the surface of the paper documents [7]. The same PIXE technique was used to trace chemical elemental composition of iron-gall inks in original deacidified rag paper from the 17th. Century, to check the efficiency of the chemical treatment. Budnar and his colleagues concluded that the technique proved to be useful for treatment decision due to the possibility of comparing chemically treated and non-treated papers [8].

This particular period seemed to be the discovery of the PIXE technique for this field. Most researchers seemed to disseminate the advantages of the technique for the preventive oxidation diagnosis of iron-gall ink documents.

To change this scenario, in 2002 the first paper appears with the use of near infrared spectroscopic reflectance imaging for non-destructive examination of works of art with different types of inks. The instrumental technique was used for an oil painting and ink drawing with good results. Near-infrared spectra of a selection of brown and black pigments were presented during the development of the investigation.

As a new technique following PIXE, the near infrared spectroscopic imaging was used again for art conservation, in the elucidation of chemical constituents of inks, in a paper written by Attas and his colleagues [9]. The technique allowed the art materials to be distinguished by their composition, and under-drawings revealed. According to the authors non-destructive identification of pigments could be used to address issues of attribution, age dating, and conservation. An additional advantage of this technique was that it can be performed off-site using portable instrumentation, and under relatively benign lighting conditions. The technique was used for the examination of a 15th. Century drawing. The authors used the technique and a color composite image produced from the images in a direct visualization of the compositional characteristics of the work. Features of

the under-drawing have been exposed, and its material tentatively identified as charcoal, by comparison with reference materials.

Differently from the human eye, some sensors introduced in photographic cameras can record data from a wider infrared spectrum. This can lead to a deviation from our natural observation; thus, camera manufacturers introduced infrared filters to limit our sensitivity to the observation of some particular colours. This technique is known as False Colour Infrared Photography and it has successfully been used by Havermans and his colleagues in the observation of iron galotanate present in the surface of manuscripts and drawings, in which the human eye did not detect colour differences [10,11]. By using this technique, the authors concluded that non oxidized parts of the ink were photographed as red, while corroded parts were photographed as black. The contribution of the technique was in the evaluation of the extension of the process of corrosion due to the presence of excess iron in writings and paintings.

In the same year, Pedersoli Júnior and Reissland compared risks involved in iron-gall ink collections, in order to help administrators to make proper decisions, based on the need for chemical or physical treatments [12]. The conclusions from this work suggested the urgent need to identify subgroups of documents in the same deterioration level for a correct decision making.

1.3. 2004-2007 – The use of instrumental analytics in documents containing iron-gall inks reaches its peak

In the year 2004 a marked increase in the number of papers published, covering distinct aspects of iron gall ink stabilization and characterization could be observed. This year can be also marked by the wide diversity of techniques and procedures used to prevent or stabilize the oxidation of iron gall inks.

This period can be considered a watershed in the investigation of chemical treatments and analytical identifications of iron gall inks. The effect of ink ingredients, the effect of chemical treatments, Fe^{2+}/Fe^{3+} ratio and more sophisticated instrumental analysis emerged during this year. Chemical constituents of the ink were tested, clarifying their contribution for the acceleration of degradation processes associated to iron gall inks.

In a particular study, authors used amylase for the removal of starch-based adhesives in order to change the migration patterns of the ink and degradation of products, with successful results in the treatment of original documents [13].

For the first time, Kolar and Strlic evaluated the effects of treatments on iron gall corroded documents emphasizing the need for a detailed study of the actual conditions of each document or group of documents [14]. Authors alerted for the urgent need to develop suitable conservation treatments, considering the large number of model papers in the world, as well as the wide diversity of ink compositions and state of conservation. Consequently, the repeatability of documents in the same condition of deterioration and subjected to the same chemical or physical treatment is low. This is an indication of the high investment of research and investigation needed to solve oxidation problems in cultural heritage.

In relation to gelatin, one of the most used sizing agents, Kolbe proved that a high content of gelatin contributes

to a better blocking and higher duration of papers; however, after aqueous treatments resizing is needed to prevent corrosion [15]. This chemical knowledge, although simple in its principle, is of fundamental importance, as most documents containing iron gall inks were sized with gelatin.

Another important constituent of iron gall inks, gum Arabic, plays an essential role in the oxidation of iron. This important binding agent was tested by Remazeilles and his colleagues in the formulation of iron gall inks for tests with cotton linters cellulose paper, without charge and sizing [16]. The effect of iron oxidation due to the presence of gum Arabic was monitored by colorimetric analysis and infrared spectroscopy. Authors concluded that gum Arabic retarded corrosion, probably due to the physical protection of the paper, thus limiting the diffusion of iron.

Proost and his colleagues investigated $16^{th.}$ and $19^{th.}$ Centuries documents by using μ-XANES technique to investigate the acid hydrolysis of the cellulose and oxidation of organic compounds due to the presence of iron [17]. The objective of the authors was to study paper disintegration by evaluation Fe^{2+}/Fe^{3+} ratio to explain the process. The authors observed considerable differences in the levels of Fe^{2+} and Fe^{3+} in documents from the $16^{th.}$ and $19^{th.}$ Centuries, confirming the suitability of the instrumental analysis determination to explain corrosion processes. Similar studies were performed by Kanngiesser and his colleagues [18].

By using in-air PIXE the elemental composition of a material can be known, when the sample is exposed to an ion beam. This technique, although complex, brings information about the knowledge of the composition of the ink to support proper conservation actions. Although not available in most laboratories the technique proved to be adequate for being sensitive and non-destructive, revealing the presence of Fe, S, K. Cu, Zn, Co, Mn and Ni in iron gall ink formulations [19].

Another sophisticated technique was implemented this year for the investigation of the *Codex major* (1600), nuclear magnetic resonance. The use of a portable device, as reported by the authors showed detailed information about the spread and extension of the deterioration process of the paper, as well as the simultaneous detection of the corrosion by iron gall ink [20].

In the end of 2004 Mossbauer spectroscopy was used to study the charge state of iron in iron-gall inks [21]. The study was performed with the use of model samples and with a manuscript from the $16^{th.}$ Century. The authors concluded that the chemical fingerprints obtained were very well established in the ancient document, but not in the recently prepared model samples. The main contribution of the technique seemed to be related to differences between chemical aspects in the core of iron-gall ink structures in comparison to the surface of the ink.

In summary, the year 2004 brought light to investigations on the composition of the inks in model samples and mainly in actual documents, through more sophisticated analytical techniques. A marked characteristic could be seen for this period: the search for a deep knowledge on the structure and composition of the inks, through non-destructive techniques, although not always available in laboratories outside academic institutions.

In the year 2005 questions related to chemical treatment seemed to be focused again. This is reasonable, since the previous year focused on the use of analytical techniques to characterize the inks in terms of their chemical

composition. In this direction, Hansen tried to improve the ageing properties of papers with iron gall inks, by interleaving them with alkaline buffer and antioxidant agents with successful results [22].

In fact, this year could be characterized as the start of high investments in the use of aqueous treatments to prevent or control iron oxidation, particularly, the use of calcium phytate solutions to remove excess iron present in non-stoichiometric preparations of iron gall inks [23-25]. Malesic and his colleagues also studied the effects of ammonium and phosphonium halides on iron gall ink corrosion, bringing important information about the size of the cation and its effect on the stabilization obtained by distinct quaternary ammonium bromides [26].

In this timeline, the year 2006 seemed to close years of exploration of the chemical characterization by classical and instrumental methods, back to a mixed range of investigation possibilities [27]. A wide range of papers, investigating from chemical characterization to more sophisticated techniques and treatment methods could be found. This seemed to be the year where iron-gall ink investigations took its place in the hall of top research, particularly for those investigators dedicated to archaeometry.

The wide diversity of themes studied during this year included an investigation of the spectrum of ink corrosion damage symptoms in the digitalization process of a large collection [28]; a detailed study of the properties affecting historical iron gall ink containing documents, both through sophisticated techniques such as PIXE and also measurements of pH of ink, grammage, absorptivity and width of ink lines, correlated to the extent of corrosion in ink [29-31].

Additionally, microspectroscopy of iron gall inks on parchments were investigated by FT- Raman spectroscopy, facing the inevitable problem of the lack of a suitable collection of Raman spectra for iron gall inks [32].

Even the synthesis of myo-inositol 1,2,3-tris- and 1,2,3,5-tetrakis(dihydrogen phosphate)s as a tool for the inhibition of iron-gall-ink corrosion was tested, with the same efficiency as the obtained when phytic salts were used for the same purpose [33].

This is a clear indication that after 10 years of investigation, it was still faced the problem of having advanced instrumental techniques, however, with drawbacks such as calibration and/or suitable reference material or an adequate databank to support the analytical available tool.

The year of 2007 seemed to be characterized by the year where investigators decided to invest their efforts towards a better comprehension of the mechanistic action of cellulose degradation due to the presence of iron-gall inks [34,35].

Havlinová and his colleagues tried an antioxidant treatment including calcium phytate (for iron oxidation stabilization) and 2,6-ditercbutyl-4-methylphenol (BHT), using both reagents in individual and combined solutions [36]. The authors concluded that the chemical action of calcium phytate was more effective than the action of BHT, because it highly contributed to an improvement in the mechanical properties and color of the paper.

With a distinct focus, Csefalvayová and his colleagues just confirmed the deleterious action of accelerated aging on Whatman paper due to the detection of acid-catalysed hydrolysis and metal-catalysed oxidation of cellulose [37]. If those results were obtained with Whatman alkaline paper, what would be expected for acid papers, probably the most abundant support of original iron-gall ink documents in the world.

In an attempt to improve the already existing calcium phytate treatment to remove excessive iron from manuscripts, Huhsmann and Hahner implemented a new method, based on calcium phytate method, known as water screen bathing, which proved to be adequate for single sheets of thin manuscripts [38]. As well, Kolar and his colleagues also investigated proved the efficiency of using magnesium phytate in place of calcium phytate to stabilize corrosion due to the presence of iron gall inks [39].

1.4. 2008-2011 – A period characterized by the implementation of international groups devoted to the study of iron-gall inks

In 2008 authors were back to laboratories, using sophisticated analytical instrumental techniques, and, in an attempt to share successful experiences, groups of researchers started to submit projects to financing agencies. The wide diversity of techniques used since then, needed to be shared and discussed, to check their suitability to specific cases, and especially what could be implemented in short and medium terms.

In that year, the use of μ-x-Ray fluorescence associated to μ-x-Ray absorption near edge structure spectroscopy confirmed, through another instrumental technique, the effects of the treatment with calcium phytate and calcium carbonate on the chemical composition of documents containing iron-gall inks, particularly the effective removal of Fe, Cu, Mn and Zn [40].

Another sophisticated and very efficient technique used by some authors was the use of infrared imaging that proved to be useful for the elucidation of an unreadable text, turned into a readable one with the use of a simple standard digital camera [41]. The technique is sophisticated, but the equipment quite easy to handle and use.

A sophisticated simple treatment (calcium phytate iron removal) was implemented this year with the determination of molecular weights and carbonyl groups content quantified for the first time. This brought a molecular knowledge of the process, not determined since then. This was possible by fluorescence labeling and GPC-MALLS, a technique that allowed the weight averaged molecular weight of particular groups involved in ink corrosion, on model and historic paper samples [42].

In this brief survey of techniques and procedures it can be realized the difficulties one would find to implement treatment methods for the stabilization of documents in a library, archive or a museum. Several questions appeared since then: Which technique to use to stabilize the ink? Where to start, in a single document or in a group of similar ones? Do I have a Chemist in my group to make this decision? Where do I find these equipments? Should I buy one of them to my lab? Is it going to work the way I think it will? Who is the professional to operate these equipments? How am I selecting the documents to start? Will I succeed in my choices?

Thinking about all those questions, some investigators started to articulate types of consortia to share successful and unsuccessful experiences in the field. At that time, the InkCor Program sponsored by the European Community, among several themes and proposals, invested in a study on the use of bromide and magnesium ethoxide in alcoholic solution to stabilize the oxidation of iron. The purpose of the group was to confront results with the use of calcium phytate [43]. Although with a very clear objective, the project specifically in this question, invested in conventional papers opening possibilities, however, to study historic papers.

Another strong group was also established this year. Researchers from Argentina, Brazil, United States of America and Cuba joined together in a working group, to create a program to disseminate knowledge, collect data about conservation and, mainly, to identify imminent needs for the field [44].

A similar idea was implemented by German groups, with successful results in the treatment of 18$^{th.}$ and 19$^{th.}$ Century manuscripts [45-46].

The year 2009 brings an important conclusion about everything what have been done in the last decade on the study of iron-gall inks. After an explosion of techniques, procedures, formation of scientific groups, it seems that the field returned to a fundamental question: Who is the person that will handle those sophisticated analytical techniques in my institution? The answer to this question was answered by Neevel who suggested a procedure that could be handled (at least, partially) by anyone interested in quantifying iron oxidation levels in documents [47]. He developed a bathophenanthroline indicator paper for iron that is used until today, without the need for specific knowledge or apparatus.

This “back to reality” new scenario found from 2009 seemed to be true, because just after the “revolutionary” and basic paper of Neevel, Banik brings a question to researchers: *Transfer of scientific research on ink corrosion to conservation practice – does it take place?* Banik at his intriguing paper states that irrespective of the approach needed to treat iron gall ink corrosion on paper documents, any decision must be based on the knowledge of reaction systems and possible inhibitors of the process [48]. This is true, according to Banik, because after more than 100 years of investigation on intervention techniques only one procedure is well established and standardized, the treatment with calcium phytate to remove iron ions. He seems to be the only researcher worried about the need to develop applied results under the guidance of conservators with sufficient scientific education. He emphasizes the need of collaboration between experts from fields other than Chemistry and Physics, as professionals of these fields must play an auxiliary role in that sort of treatment.

This year is clearly characterized by the development of simple and basic techniques, such as iron testing, measurement of pH, treatment with small amounts of water, use of coating tissues with gelatin [49].

Another confirmation for this fact can be found in the work of Hanus and his colleagues [50]. They used documents from the Slovak Republic, classifying and evaluating their conservation state, according to their pH, stage of ink migration, presence of iron and/or copper and prevalence of brown or black colour. As can be seen, all those analytical tools, widely used, but just for model papers and inks or individual documents, seem not to be efficiently transferred to a real application for archives, libraries and museums.

As if it were an introduction to what was expected for the forthcoming year, still in 2009, two papers were published restoring instrumental techniques to treat or to interpret the process of corrosion derived from iron gall inks [51, 52].

Years from 2010 until 2015 seemed to be the least fingerprinted years for iron-gall ink studies. A survey of the published literature did not reveal a typical aspect covering the period, although it cannot be neglected the high number of scientific papers with the use of instrumental analysis, but, with limited interest or application. Some examples include: In 2010, it could be found the use of μ-X-ray fluorescence for archaeometry and conservation science [53], μ-FTIR [54], gas chromatography and mass spectrometry [55], near-infrared spectroscopy [56].

In continuation, the forthcoming year of 2011 brought an important contribution for the field. The creation of "The Iron Gall Ink Website" (irongallink.org), created by the Cultural Heritage Agency of the Netherlands, with the participation of several countries in Europe and outside the continent. How to make the ink, classical recipes, how to treat documents, which strategy to implement are information one can reach from the site, free of charge.

1.5. 2012-2015 – What to do with so many techniques? How to transfer this knowledge to a practical large-scale treatment?

From 2012 until 2015 a huge amount of papers were published. Which technique prevailed for the diagnosis, treatment or recovery of iron gall inks or iron gall ink documents? One may choose: size exclusion chromatography [57], FTIR [58]; classical treatments or diagnosis to study the effect of parameters on the diffusion of sulphate ions [59]; UV/VIS, FTIR and EPR techniques, as well as nanospray ionization mass spectrometry, for localized chemical analysis [60-62]; scanning electron microscopy [63]; finally, in this five-year period, the use of Mossbauer spectroscopy [64], X-ray spectroscopy [65] and atomic absorption spectrometry in the elucidation of the kinetics of iron removal from iron gall inks [66].

To finish 2015, Manso and his colleagues provided interesting information about "the mysterious halos in iron gall ink manuscripts", clear inhibiting agents for microbes on papers [67]. This is an indication that not always, chemical and microbiological contamination does not compete, but clearly interfere one on another.

2. Conclusions

The year of 2016 brings a lot of information about techniques and new methodologies for the treatment and stabilization of documents containing iron-gall inks [68-79].

Where do researchers in the field intend to go? Should they go to basics of Analytical Chemistry or to the most advanced instrumental techniques available? How many questions should we ask to get a final decision on how to act in a specific archive, document, book or painting with clear signs of oxidation? The wide diversity of possibilities opened in these last 20 years indicate that we have accumulated a huge amount of knowledge, but we still don't know how to use those information in a practical manner. In the next years efforts should be made to protocol procedures, to standardize procedures and mainly to establish conditions suitable for groups of

documents with similar characteristics. Sometimes we spend too much effort on a single document with an outstanding importance which deserves specific treatments, based on its historical or scientific importance. But this is not the reality of most of our documents. Most of them have its importance, but how much will cost to treat one by one? We should share these questions with archivists, librarians and historians. By sharing this responsibility, we also save technology from being misused and criticized for spending efforts and money on a cause we are not sure deserves such investment.

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