

## Pages of Poison Identifying 19th Century Arsenical Green Books at Queen's University Library

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### Résumé de l'article

Au 19<sup>e</sup> siècle, l'arsenic était un additif et un colorant couramment utilisé dans le papier, les vêtements, les articles ménagers, les produits personnels et même les confiseries. Bien que la plupart de ces produits toxiques aient depuis longtemps été retirés de la consommation publique, les livres créés à l'aide d'acétoarsénite de cuivre, un pigment vert, restent dans nos bibliothèques et collections personnelles, avec des implications potentielles pour la santé. Cet article se concentre sur l'identification de livres du XIX<sup>e</sup> siècle dans la Bibliothèque de l'Université Queen's, à Kingston, soupçonnés de contenir de l'acétoarsénite de cuivre ou du vert émeraude. Sur la base d'une identification visuelle, 150 livres publiés entre 1797 et 1900 ont été sélectionnés dans les collections pour des tests de spectroscopie de fluorescence X (SFX) afin de détecter le colorant arsenical. Les résultats ont révélé que 28 livres testés contenaient des quantités importantes d'arsenic dans leur tissu, leur papier de couverture, leur décoration de surface, leurs pages de garde ou leurs avant-bords.

Ces résultats soulignent la nécessité de mettre en oeuvre des protocoles de manipulation et de stockage appropriés et des stratégies de conservation pour atténuer le risque d'exposition à l'arsenic pour le personnel des bibliothèques, les chercheuses.eurs et les usagères.ers. De plus, cette recherche contribue à une compréhension plus large de l'impact de l'arsenic sur la préservation du patrimoine culturel, soulignant l'importance de la collaboration interdisciplinaire entre bibliothécaires, conservatrices.teurs, archivistes, historien.ne.s et scientifiques. En documentant et en traitant la contamination à l'arsenic dans les collections des bibliothèques, les institutions peuvent préserver le bien-être des personnes qui interagissent avec ces documents tout en préservant ces éléments du patrimoine culturel pour l'avenir.



Queen's University

Queen's University

*In the 19th century, arsenic was a commonly used additive and colourant found in paper, clothing, household goods, personal products, and even confectionary items. Although most of these toxic products have long been removed from public consumption, books created using copper acetoarsenite, a green pigment, remain in our libraries and personal collections, with potential health implications. This article focuses on identifying 19th-century books in the Queen's University Library, Kingston, suspected to contain copper acetoarsenite or emerald green. Based on visual identification, 150 books published between 1797 and 1900 were selected from the collections for X-ray fluorescence (XRF) spectroscopy testing to detect the arsenical colourant. Results revealed that 28 books tested contained significant amounts of arsenic in their bookcloth, covering paper, surface decoration, endpapers, or fore-edges.*

*These findings underscore the necessity to implement proper handling and storage protocols and conservation strategies to mitigate the risk of arsenic exposure to library staff, researchers, and patrons. Moreover, this research contributes to the broader understanding of arsenic's impact on cultural heritage preservation, highlighting the importance of interdisciplinary collaboration between librarians, conservators, archivists, historians, and scientists. By documenting and addressing arsenic contamination in library collections, institutions can safeguard the well-being of individuals interacting with these materials while preserving these cultural heritage items for the future.*

**Keywords:** arsenic · bookcloth · emerald green · 19th century · special collections

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**Mots-clés :** *arsenic · collections spéciales · toile à livres · vert émeraude · XIXe siècle*

**D**URING the 19th century, arsenic was a common ingredient in household goods and could be found in everything from clothing to wallpaper and insecticides (Hawksley 2016). Arsenic was also used to colour bookcloth, enticing buyers with attractive, fashionable, bright green covers. Studies to detect arsenical bookbindings in library collections have been undertaken internationally (Alvis 2018; Holck and Rasmussen 2018; Delbey et al. 2019; Tedone and Greyburn 2020, 2022, 2023; Vermeulen et al. 2023); however, comparative research has not yet been done in the Canadian milieu. It is important that Canadian libraries become involved in the newly developing field of bibliotoxicology<sup>1</sup> (Grayburn and Tedone 2023) for many reasons, including:

- developing diversity in expertise regarding understanding potential hazards and creating safer practices for managing collections;
- sharing resources, which allows for greater access to funding and equipment; and
- collecting and disseminating data specific to the Canadian library and publishing context, both within the country and internationally.

Situating the findings within the technological changes of the book trade in the 19th century that importantly resulted in the mass production of these books, this

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1. Bibliotoxicology is “the study, analysis, and management of potentially toxic materials in library and archives collections” (Poison Book Project 2024).

paper outlines the process used to identify arsenical bindings in the W.D. Jordan Rare Books and Special Collections at Queen's University. The need to undertake this work came to light in December 2018, when a follower of the W.D. Jordan Library Instagram account (@jordan\_library) asked if the bookcloth in a posted image contained arsenic. Prior to this inquiry, the possibility of items containing toxic pigments potentially harmful to those who handled the books had not yet been considered by library staff. By sharing the methods used to identify toxic pigments in museum collections, it is hoped that other institutions will be able to locate arsenical items in their collections effectively. Additionally, recommendations are provided to minimize the health and safety risks associated with the ongoing handling, long-term storage, and care of identified arsenical books for library employees and researchers.

Upon commencement of this research, approximately 150 books and other archival materials, including stereographs, were selected through visual identification of the covers, endpapers, and fore-edges with an emerald green colour swatch bookmark acquired from the Poison Book Project (2024). Using X-ray fluorescence (XRF) spectroscopy, it was possible to determine if the books contained emerald green pigment. XRF is a non-invasive analytical technique that allows for the rapid and accurate detection of arsenic, providing valuable insights into the composition of historical bookbinding materials without causing harm to the artifacts. The presence of arsenic was identified by testing various areas of the book bindings and paper surfaces. Positive results for copper acetoarsenite were found in the W.D. Jordan Rare Books and Special Collections, including in bookcloth, covering papers, surface decoration, endpapers, papers, fore-edges, and the decorative paper of stereographs.

Discovering the existence of arsenic in libraries and special collections is critical to preventing potential health hazards for staff, researchers, and the public. Arsenic exposure has been associated with many health problems, such as skin irritations, respiratory complications, and cancer (National Institute for Occupational Safety and Health 2019). Currently, no known arsenic levels can be considered entirely "safe" regarding arsenical pigments in bookcloth and paper. This is due to the fact that toxicity can be acute or cumulative, and exposure levels need to be calculated on an individual basis based on body weight, natural resistance to arsenic, and many other factors (Tedone and Grayburn 2023). While the risk of arsenic exposure from handling arsenical books is generally low, it remains an issue due to the potential for a gradual buildup of arsenic in the body over time, especially for those who frequently interact with these materials, such as archivists, librarians, conservators, and researchers. By pinpointing books containing arsenic and implementing appropriate

handling procedures, libraries can reduce the possibility of arsenic exposure and ensure the well-being of their visitors and employees.

Furthermore, studying the prevalence of arsenic in 19th-century bookbinding materials and other paper-based collections holds significant value in gaining insights into historical manufacturing practices and their implications for preservation endeavours. Identifying, documenting, and addressing the presence of arsenic in books can help libraries and institutions formulate effective conservation strategies to safeguard their collections for posterity.

This research makes a valuable contribution to understanding arsenic contamination in library collections and emphasizes the need for collaboration among researchers, librarians, and conservators to safeguard cultural heritage and public health. The findings highlight the importance of further studies to identify other sources of arsenic and heavy metal contamination in historical materials collections and stress the importance of educating the library sector about potential bibliotoxicological harms.

## Literature Review

### ***Emerald Green in the Victorian Home***

During the early Victorian period, many new synthetic pigments used to dye textiles and colour papers were produced industrially for the first time. These bright and bold colours quickly became highly fashionable. Copper acetoarsenite, commonly known as emerald green, was one such colour. First synthesized in the lab around 1800 in Schweinfurt, Bavaria, emerald green came into commercial use in 1814 (Tedone and Greyburn 2022). Due to the presence of arsenic, emerald green (also sometimes called Schweinfurt Green, Paris Green, Vienna Green, or King's Green) is acutely toxic through ingestion and inhalation. When looking at any green items dated from the Victorian era, whether covering a book, a wall, or a dress, the distinctly bright, yellowish-green colour can strongly indicate that the item contains toxic arsenic-based colourants.

One of the most prominent and well-documented areas where arsenical green pigments were used during the Victorian era was in wallpapers (Hawksley 2016). Despite Victorian cultural ideals that the home should be a sanctuary for family members, the environmental dangers from items inside of the home made it a less-than-ideal haven (Bartrip 1994). The first written warning about the dangers of arsenic used in wallpaper occurred in 1843 by Dr. Gmelin (*Scientific American* 1873). Physicians of the time knew that arsenic found in everyday items made people sick and could result in death. However, the wallpaper manufacturing industry was



highly profitable, so there was little interest in stopping the practice (Hawksley 2016). Accidental arsenic poisonings were also documented during this time. Accounts included a child chewing on a book covered in arsenical paper and a member of a kitchen staff mistaking some white powder, which turned out to be arsenic, for flour (Whorton 2010). Books, such as Alfred Taylor's *On Poisons, in Relation to Medical Jurisprudence and Medicine*, published in 1848, clearly identify the dangers of arsenic and, as in Taylor's case, examine poisons through the lens of forensic toxicology.

Of course, accidental poisonings from inadvertently encountering arsenic-tainted items were not the only means of injury or death. Arsenic "reigned throughout the century as the poison of choice for committing homicide" (Whorton 2010, vii). Despite all the evidence, unintentional and intentional poisons continued well into the 1850s until the Arsenic Act of 1851 was passed by parliament in the United Kingdom. However, the act did not prevent arsenic from being used in household products, and it continued to be readily available. Published in 1862, a cartoon titled "The Arsenic Waltz" depicting two skeletons, one wearing what is presumably a toxic gown, was published in *Punch* (a popular British weekly magazine of humour and satire), illustrating the cost of wearing clothing dyed with arsenic – literally dancing with death (figure 1). It is a visual commentary on the toxic elements prevalent in everyday life in the 19th century and demonstrates that the dangers of arsenic were well-known at the time. Although most products containing arsenic have been removed from public consumption today, they do remain in our libraries, galleries, and museums.



**FIGURE 1** A cartoon appearing in the popular humour magazine *Punch, or the London Charivari* (February 8, 1862) titled "The Arsenic Waltz." The caption reads, "The new dance of death. (Dedicated to the green wreath and dress-mongers.)" Image courtesy of Stauffer Library.

## *The Changing Victorian Book Industry*

Pressures to transform into large-scale industries, including increasing manufacturing capacity during the Victorian era, also affected the book trade. For almost 400 years, the production of books stayed relatively the same. This was mainly due to material costs and labour, as all components of the book, including the paper, the thread, and the binding, were produced by hand. Because of this, bookbinding was slow, meticulous work. However, increasing demands for books by a growing literate population meant that booksellers were looking for new ways to produce books quickly and sell them cheaply. Three innovations were required before this could be possible. First was the development of an inexpensive bookcloth suitable for binding that could adhere to the boards without the glue showing through. Secondly, book covers needed to be manufactured in large numbers. This led to the invention of the case binding. In the case binding process, large numbers of covers were created and attached to the text blocks, resulting in mass-produced, identical books. Finally, adding gold stamping to the bookcloth rather than hand tooling, beginning in 1832, forever changed the production of books (Allen and Gullans 1994) and opened the stage for publishers' bindings. It is unlikely that emerald green would have found its way onto the covers and pages of the common book if not for the advent of the identical, mass-produced, cloth-covered publishers' bindings.

### *Publishers' Bindings<sup>2</sup>*

The story of publishers' bindings begins with a humble piece of cloth and two pioneering Britons looking to solve a handful of business-related problems. In the first quarter of the 19th century, William Pickering, a London publisher, and Archibald Leighton, a binder, wished to produce and sell books in large quantities. Products of their time, these two men sought to incorporate three key elements of England's rapidly industrializing landscape in the production of printed materials: repeatability, consistency, and scaled production. For that to happen, Pickering and Leighton understood that some not-so-humble materials on which bookbinders had previously relied would have to be jettisoned. Before the 1820s, most books were sold in quires (gatherings or sections), with temporary paper wrappers or board bindings meant to be bound by the purchaser. Leather was the most popular covering material, but it was expensive, and the bindings crafted reflected the taste and budget of the buyer. Various cloth coverings, such as silk, velvet, and canvas (quite common on school texts), had undoubtedly been used previously, but chiefly as specialty bindings arranged by the purchaser or the retailer in limited quantities for a quick sale. Bespoke bindings such as these were unique to the individual book and binder.

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2. This section draws extensively from Kim Bell's unpublished Master's thesis *Speaking Volumes: Publishers' Bindings in English-Canada 1870-1920*, completed at Queen's University in 2020.

Pickering sought to provide an increasingly literate public with a durable binding that was less expensive than leather yet more pleasing to the eye than paper. Canvas was not a viable option due to its coarse texture and lack of flexibility. It was also prone to fraying and wear, especially along the board edges and spine. The finer fabrics were expensive to work with and often susceptible to “strike-through”—where the binder's glue showed through the material. To prevent this and strengthen the fabric for binding and decoration, Leighton had to size the fabric, probably using a starch filler. Sizing reduces the fabric's porosity, making it easier to manipulate during manufacturing processes. Sizing fabric involves applying a substance or treatment to enhance its properties, such as strength, smoothness, and resistance to moisture. The process involves coating the fabric with a sizing agent, typically made from starch, gelatin, glue, or synthetic polymer.

Critically, none of this was possible without another innovation that allowed for an attractive, inexpensive binding: case bindings. Case bindings were manufactured in large numbers, concurrently and independently from the text block, and subsequently glued to the book, making it economically feasible for the publisher to bind in mass quantities.

Nor was the case binding the only technology that helped Pickering along. Further enhancements were made to cloth texture in the 1830s, with ribbon embossing resulting in more appealing covers. However, this technique was expensive, and its use soon faded to be replaced by other decorative means. As a means of blocking the cloth in gold, the introduction of the Imperial arming press in 1832 made a lasting impression (Ball 1985). To begin with, blocking in gold only appeared on the spines, but this soon gave way to greater use. Central vignettes, blocked in gold on the upper boards, added visual interest to the covers, and these pictorials, frequently framed with borders, made their way onto both boards in the 1840s. This innovation paved the way for the use of various decorative materials and techniques, including the application of arsenic-based paints. These vibrant pigments were prized for their bright, eye-catching colours, enabling publishers to produce books with richly adorned covers that stood out in the marketplace.

Scholarly literature on publishers' bindings, a predominantly British and American phenomenon, is extensive. Surveys that examined bindings and published lists of cover designers provided the foundation for the work that would follow. Sadleir's *The Evolution of Publishers' Binding Styles*, considered the foundational study of publishers' bindings, introduced the topic using examples from British publishers through a bibliographer's lens (Sadleir, 1990). Indeed, Sadleir, writing in 1930, acknowledged in the introduction that the topic was so new that “it does not altogether belong either to the history of publishing or to the history of book-



manufacture” (Sadleir 1990, 1). Despite this uncertainty, Sadleir provided an initial rendering of the evolution of publishers' bindings within the British context.

Other works followed, discussing American and British binding styles and providing research into the technology and development of the book trade. Book history scholars were researching bindings in new ways. Mirjam Foot used the vast holdings of the British Library to link book production and bindings to questions of authorship, publishing, reading, and collecting, effectively bringing bookbinding to the forefront (1999). While continuing with similar themes of listing bindings by marking the evolution of binding designs and their designers, Foot also connected the bindings to the society from which they emerged, arguing that the covers did more than merely protect the text. Approaching the subject from the bibliography perspective, as did Sadleir, Foot broadened the focus, considering the bindings from within the production cycle and beyond their aesthetic value while stressing the importance of the binding structure as evidence. Pre-1820 bindings, separate as they were from the production of the text, told a different story than did publishers' bindings.

### ***Arsenic in Books***

Jakob Povl Holck, a research librarian, and Kaare Lund Rasmussen, an associate professor in the Department of Physics, Chemistry, and Pharmacy at the University of Southern Denmark, published a 2018 blog post about the discovery of arsenic-laced paint covering 16th and 17th-century books in the library collection (Holck and Rasmussen 2018). The three books were covered with pieces of medieval manuscripts, a common practice at the time. These covers were, in turn, coated with green paint in an effort by the binders to obscure the reused parchment. Initially, the researchers wanted to uncover the Latin text obscured under the green paint. The results of the XRF analysis revealed that the green paint contained arsenic. Further investigation revealed that the green-coloured pigment contained a mixture of orpiment (a yellow arsenic-based pigment) and indigo (a blue dye) rather than emerald green (copper acetoarsenite). It was therefore determined that the green paint was part of the original binding process, not added hundreds of years later, as the researchers initially thought (Delbey et al. 2019).

Shortly after the discovery at the University of Southern Denmark, Alexandra Alvis, a librarian at the Smithsonian, discovered a 17th-century book containing arsenic in the Cullman Library (Alvis 2018). XRF determined that this book also contained orpiment and indigo, the same chemical composition that Holck and Rasmussen discovered in the books they analyzed. Early bookbinders likely aimed to

make books aesthetically pleasing to the paying customer, much like the bright green bindings found later in the 19th century.

Tedone and Grayburn used publishers' bindings as the basis for their research on the use of arsenic in bookcloth during the 19th century. When preparing an item to go on exhibit at the Winterthur Library, located in Winterthur, Delaware, Tedone took note of the bright green cloth, a red flag for arsenic used in the Victorian era and tested the cloth for arsenic (Tedone and Grayburn 2020). The positive results then prompted a survey of the collection to determine if other items contained the toxic element. Using XRF and Raman Spectroscopy analysis, over 400 volumes were tested for copper acetoarsenite, and thirty-eight items with prominent levels of arsenic and copper were found (Tedone and Grayburn 2022). This research resulted in the creation of several best practices for testing books for arsenic and included suggestions for the safe handling of arsenical books. The *Arsenical Books Database* was created and shared online so institutions could cross-reference their holdings with those books already known to contain arsenic.

### ***Analytical Testing for Arsenic and Copper in Rare Books and Cultural Heritage Collections***

A wide-range of methods may be employed to test for arsenic and copper. However, many are not appropriate for use within rare book and cultural heritage collections due to their destructive nature which would permanently alter, mar, or destroy parts of the books tested. For this reason, only non-destructive analytical testing was considered. Researchers thus far have focused on three types of non-destructive testing including Raman spectroscopy, XRF, and visible near-infrared spectrometry (vis-NIR).

Raman spectroscopy, a non-destructive analytical method, is a safe and precise way to detect arsenic-based compounds commonly found in 19th-century pigments and dyes, particularly in bookbindings. Clark's 1999 study demonstrated Raman spectroscopy's efficacy in detecting arsenic-containing pigments like emerald green. Further research by Smith, Baker, et al. and Smith, Brooks, et al. (2002) highlighted the advantages of Raman over traditional methods such as XRF and mass spectrometry. Raman provides detailed molecular information and can differentiate between various chemical compounds, including arsenic compounds. This specificity is critical in conservation science, where understanding the exact composition of materials is essential for developing appropriate conservation interventions. Recent advancements have improved the sensitivity and portability of Raman instruments, enabling non-destructive on-site analysis of valuable or fragile items. Tedone and Grayburn (2020, 2022) extensively explored the application of Raman spectroscopy for the analysis of arsenical books. Their study highlighted the advantage of Raman

spectroscopy in providing molecular-level information, enabling the precise identification of hazardous compounds in books.

Vermeulen et al. (2023) employed XRF as the preferred tool for the first step in identifying arsenical pigments and was also employed by Tedone and Grayburn (2020, 2022). XRF is a widely adopted technology used heavily by geologists to analyze rock, soil, and sediment samples and by engineers and the construction industry, where it can determine the compositions of metal alloys and cement. XRF is also heavily used in the field of art conservation, as it is a preferred non-destructive analytical technique for elemental analysis (Bezur et al. 2020). That is, the elements present in a book's covering material can be analyzed without removing any sample material or causing damage to the book. To use an XRF in Canada, you must hold an operator's certificate by completing a training requirement and passing a written exam. Natural Resources Canada administers the licensing process (Natural Resources Canada 2024).

Recently, Gil et al. (2023) used visible near-infrared spectrometry (vis-NIR) as a cost-effective and efficient tool for identifying emerald green in book bindings, representing an exciting development in the field of bibliotoxicology. XRF and Raman can often be prohibitively expensive, especially for smaller institutions, and require specialized training and protocols. As Gil et al. (2023) noted, vis-NIR has no safety requirements and is a less expensive option. The technique offers a rapid and non-invasive method to assess books' organic and inorganic components. While still under exploration, vis-NIR holds the potential for comprehensive analysis without some of the drawbacks and limitations of XRF and Raman.

As technology advances, the refinement of vis-NIR and its combination with other methods may offer even more precise and cost-effective insights into the composition and condition of 19th-century bookbindings. Testing library bindings, regardless of the technology used, will likely require institutions to collaborate with local experts with access to these tools or utilize the services of the Canadian Conservation Institute (CCI).

## Method

### *Identification and Selection of Book Titles for Analysis*

A multi-pronged approach was used to select books to be tested. A running list of titles and their associated information was started in a spreadsheet and any book identified from the 19th century with a bright green cover was added to the file for future testing. Additionally, the *Arsenical Books Database*, which identifies books that had previously tested positive for arsenic at other institutions, was compared against

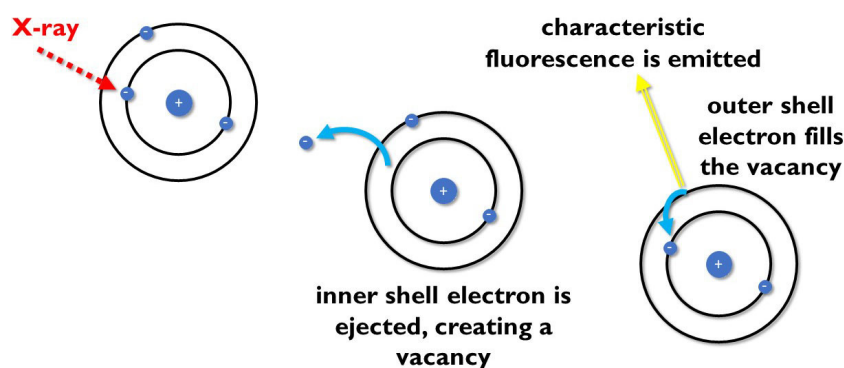
the Library holdings (Poison Book Project 2024). Four items from this list matched holdings in the Jordan Collections. The broader selection of books was accomplished through visual inspection of the stacks for books bound in green cloth and published between 1820 and 1900. Additionally, the Poison Book Project identification bookmark (Poison Book Project 2024) aided in the visual identification of suspected, green-bound materials. If the book fulfilled these two criteria, it was removed to a cart for testing. Staff started with the children's collection, which is known for its large number of publishers' bindings, comparing each book with the green colour swatches on the bookmark.

Eventually, the physical search moved into the rest of the library collections and the scope was expanded to include bright green paper bindings (which tend to have earlier publishing dates), fore-edges, endpapers, and decorative painted covers. Although the study primarily focused on books published between 1820 and 1900, one ten-volume set of books published between 1797 and 1810 was also tested as the green fore-edges on these books matched very closely to the swatch on the bookmark. Visually identified books with a pre-1820 publication date may have been bound or rebound between the 1820 to 1900 timeframe and in this instance, the set was included in testing. Although outside the primary date range, these earlier volumes require the same careful identification, storage, and handling protocols to ensure safety. Lastly, stacks in the circulating collections were searched for potential arsenical material. The selection process for these books included visual identification and fitting within the target date range. However, library staff also focused on Library of Congress classification areas that returned significant numbers of potential items in the special collections. As a result of the selection process, approximately 150 books were identified for testing.

### *Portable X-ray Fluorescence (pXRF) Spectroscopy*

To determine the composition of the green colourant present, pXRF analysis was chosen as the analytical identification method. Although the Poison Book Project bookmark, along with publication date information, aids in detecting potentially arsenical books, it does not provide definitive results. In contrast, pXRF has been previously proven efficient and accurate for identifying copper acetoarsenite present in emerald green bookcloth (Poison Book Project 2024), and the conservator had prior experience employing the technique. Additionally, through collaboration with the Department of Art History and Art Conservation, it was possible to bring the pXRF into the Jordan Library, where the books could be tested without having to leave the special collections. This made testing easier as lengthy loan reports and other paperwork related to external borrowing did not need to be completed.

XRF technology works to identify copper and arsenic by directing a small amount of X-rays at a sample. The sample is affected when the X-rays reach an electron near the nucleus. The X-ray causes the inner electron to be ejected or knocked away. When this occurs, the atom becomes unstable, and an electron from an outer orbital moves into the inner orbital to stabilize itself, emitting a photon of light or fluorescence. Because each atom in the periodic table has a characteristic fluorescence wavelength when the XRF captures the wavelength, it generates spectra that can be used to identify the specific elements present (figure 2).



**FIGURE 2** A diagram illustrating how XRF analysis determines the elemental composition of materials. Image created by Robin Canham.

The XRF setup used for the analysis of selected books at Jordan was uncomplicated, as the books were stable and did not exhibit any condition issues hindering the ability to test them safely. The Bruker Tracer 5i portable XRF spectrometer was set up in the Special Collections Conservation Laboratory. The XRF, with the 8 mm collimator, was connected to the desktop stand with the sample stage accessory placed on top (11.4 mm x 10.0 mm in dimension). This allowed the books to be gently placed upon the sample stage and fully supported while testing. The XRF settings were 40kV voltage, 9.6µA anode current, 25 µm Ti/300 µm Al wheel, and 30 seconds live time irradiation (figure 3). The XRF settings were determined through consulting previous research for best practice (Tedone and Greyburn 2020; Vermeulen et al. 2023).





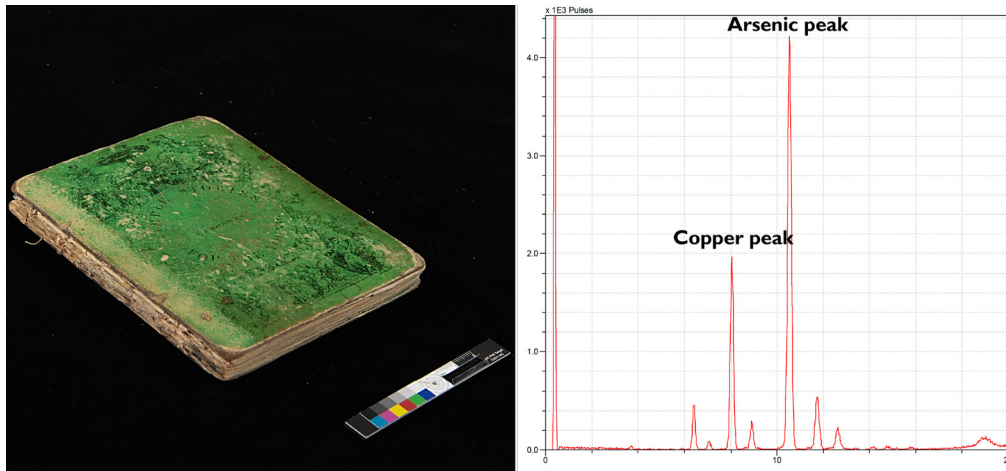
**FIGURE 3** Photograph depicting the pXRF setup. Books were placed on top of the sample stage accessory for testing. Photo credit: Robin Canham.

The Bruker Tracer 5i features an internal sample camera, which was used to identify the measurement positions. This was especially useful when analyzing books with substantial amounts of gold blocking or books with significant surface abrasions, as it allowed for visual pinpointing of highly pigmented areas for testing.

Testing began with books currently known to contain arsenic, as indicated by the *Arsenical Book Database* (2024). Once the results from the known items indicated strong spectral peaks for copper and arsenic, the remaining books were tested.

## Results and Analysis

Bruker ARTAX software was used to examine the captured spectra. Using the software, the spectra for each book are presented in a graph, with peaks corresponding to specific elements. Strong peaks for copper and arsenic can signify the presence of copper acetoarsenite. For example, the resulting spectra for *Simple Stories for the Amusement and Instruction of Youth* had high peaks that correspond with copper and arsenic (figure 4).



**FIGURE 4** (Left) Photograph of the front cover of MacDonald, W.R. *Simple Stories for the Amusement and Instruction of Youth*, London: Darton & Clark, 1842, Queen's University, Special Collections, Child PZ5 no.1324. (Right) The XRF spectra of the green paper cover demonstrate high peaks for copper and arsenic atoms, as seen in the Bruker ARTAX software. Photo credit: Robin Canham.

Of the approximately 150 books tested, 28 titles contained significant spectral peaks where copper and arsenic were found together. This comprised 18% of books selected for testing. Although the publishing dates used in the selection process were from 1820-1900, the books found to contain emerald green ranged from 1797 through 1870. Further investigation and research into the earlier dated books must be completed to determine if these books were bound contemporary to their publishing dates or later. No Canadian publisher examples were found among these items. However, books published in England, Ireland, Scotland, Italy, and the United States were identified. This outlines the wide international use of arsenic as a colourant in the book publishing trade. Four titles found to contain arsenic were part of the circulating collection and were subsequently removed from circulation and housed in special collections.

Copper acetoarsenite was found to be present in bookcloth, but it was not limited to this solely. Covering paper, painted surface decoration, endpapers, and fore-edges were also found to contain arsenic. This demonstrates that the use of emerald green as a decorative element in the book trade was widespread and not limited to the book cloth or textile industries. For the four titles identified that were bound in bookcloth, the bookcloth on the spines had faded to a dull brownish colour, as seen in the example of *The Life of Gerald Griffin* (figure 5).



**FIGURE 5** Photograph of Griffin, Daniel, and Gerald Griffin. *The Life of Gerald Griffin*. By his brother. [32d ed.]. Dublin: James Duffy 1872, Queen's University, Special Collections, PR4728.G8 Z63 1857t. Note that the bookcloth on the spine has faded to a dull green colour. Photo credit: Robin Canham.

For the remainder of the materials that tested positive for emerald green, two titles were found that were bound in coloured paper, twelve titles that had coloured fore-edges (figure 6), and two titles that had coloured endpapers (figure 7). The emerald green endpapers exhibited designs similar to those of ribbon-embossed bookcloth (Krupp 2008). These two books had the same provenance and were formerly in the Royal Library in Naples, which an Italian noble family owned. The bright green endpapers stand out from the red leather covers embossed with the Royal Bourbon coat of arms.



**FIGURE 6** Photograph of *Politisches Taschenbuch fur das Jahr 1830*, Hamburg: Hoffman und Campe, 1830, Queen's University, Special Collections, Mini JA55.P6 1830. Note the arsenical green fore-edge colouring. Photo credit: Robin Canham

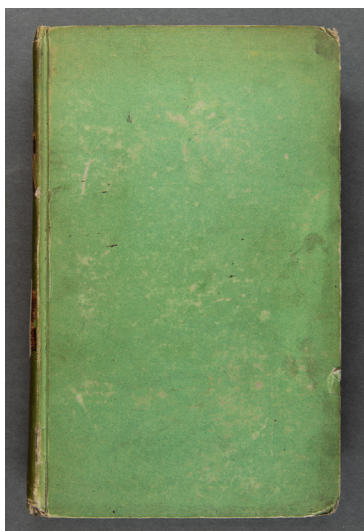


**FIGURE 7** Photograph detailing the front ribbon embossed arsenical green endpapers of *Atti Della Reale Accademia Delle Scienze, Sezione Della Società Reale Borbonica*, Napoli: Reale accademia delle scienze 1851, Queen's University, Special Collections, Q54.A894t. Photo credit: Kim Bell.

The list of items that tested positive for copper acetoarsenite and the spectra were shared with the Poison Book Project, and the results were added to the *Arsenical Books Database*. This will assist others attempting to identify potentially toxic books in their collections in the future. A complete listing of these titles found at W.D. Jordan that are highly suspected to contain emerald green pigment can be found in Appendix 1.

#### ***Possible Evidence of Arsenic Applied as a Pesticide Treatment***

A subsequent interesting finding was discovered in two books covered in the paper titled *Constitutions de la Nation française, Vol. 1 & 2* (1819) (Figure 8). This set had a high amount of arsenic present. However, the expected amount of copper present was much less than what was measured. This suggests that the green colour of these two books may have come from a different copper-based pigment, possibly copper carbonate, rather than copper acetoarsenite. This could mean that the presence of arsenic was not due to the presence of emerald green but instead to a pesticide treatment applied to the books in the past. Further analysis of these two books is necessary to further explore this conclusion.



**FIGURE 8** Photograph of the green paper cover on *Lanjuinais, J. D. (1819). Constitutions de la Nation française*. Baudouin, Queen's University, Special Collections, JN2501.L3Vol.1. Photo credit: Robin Canham.

### ***William Notman Stereoscope Cards***

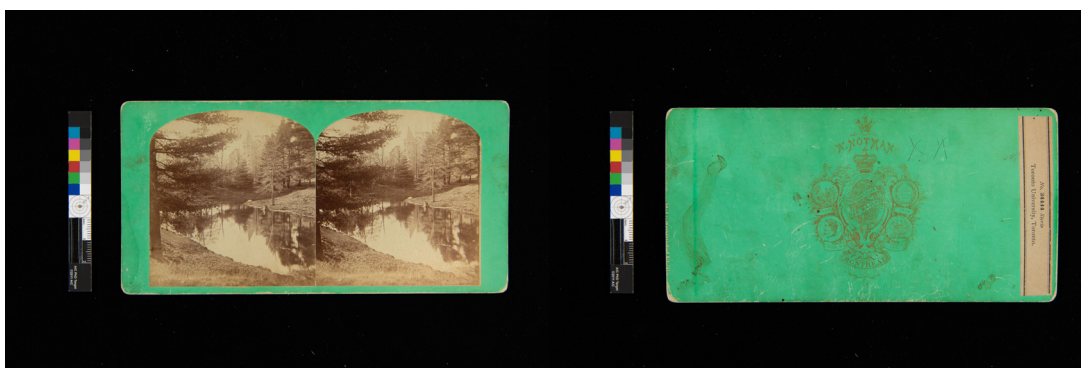
Another interesting finding of particular interest to Canadian libraries, archives, and museums was the discovery of copper acetoarsenite on stereoscopic views from the studio of well-known 19th-century Scottish-Canadian photographer William Notman. Notman was famous for his pioneering work in the field of photography during this time, especially for his contributions to portrait photography and his documentation of Canadian history. At his Montreal studio, Wm. Notman & Son grew to thirty-five employees by 1864, and his landscape and cityscape photographs of Canada provided critical historical records of the country's development (Parsons 2014).

In the summer of 2023, and as the testing of the green books was taking place, W.D. Jordan Library was presented with a donation of an impressive collection of over 10,000 stereoscopic cards. Among them were cards created by Notman (figure 9). Upon close examination, it was observed that several of the stereoscope photographs were supported by arsenical green-coloured paper adhered to a card, a suspicion that was subsequently verified through XRF testing. Additional research is necessary to ascertain the magnitude of arsenic usage in 19th century stereoscope cards and identify those that Notman produced.<sup>3</sup>

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3. The Authors have subsequently published on their stereograph research. See: "Toxicity in 3D: XRF Analysis for the Presence of Heavy Metals in a Historical Stereograph Collection at Queen's University Library, Canada" in *Studies in Conservation*: <https://doi.org/10.1080/00393630.2025.2450976>.





**FIGURE 9** Photographs of a William Notman stereograph view circa 1870s, Queen's University, Special Collections. (Left) Recto view. (Right) Verso view. Photo credit: Robin Canham.

### ***Development of Health and Safety Protocols at W.D. Jordan Rare Books and Special Collections***

Based on the results of the research and the confirmation through XRF analysis that 28 books and additional stereoscope slides were comprised of arsenic, and it was likely that more arsenical titles were present in the circulating collection, a reference guide for identifying arsenical titles was developed and communicated with staff (Appendix 2) along with our identification bookmark that was developed based on the idea presented by the Poison Book Project.

Recommendations for safe handling and ongoing care of items containing emerald green pigments were also developed and communicated to staff. Generally, the guidelines established by the Poison Book Project were followed, with the needs of the library taken into account. Determining the recommendations for safe handling at W.D. Jordan involved several key considerations. The frequency and duration of handling these books were factored in, with more stringent guidelines recommended for individuals such as conservators interacting with these materials in a more involved context. Additionally, the practicality of implementing these recommendations was assessed. W.D. Jordan Library has the space to relocate the items to a separate area, but this might not be feasible for other institutions. Digitizing the items was carefully considered as a way to minimize direct handling and reduce exposure risks. However, the idea was ultimately rejected due to insufficient staffing levels. The process of safely digitizing these materials would require specialized handling procedures and significant time investment, which current resources could not support. As a result, the focus remained on implementing safer handling protocols for physical access. Recommendations included:

1. All books containing arsenic or suspected of containing arsenic should be handled with nitrile gloves. Hands should be thoroughly washed after handling, even if gloves are worn.

According to Gladle (as cited in Tedone and Grayburn, 2020), "There are no safe exposure limits for copper acetoarsenite, so limiting direct contact, inhalation, and ingestion of bookcloth pigment insofar as possible is essential" (2020, 110). The recommendations developed at Queen's University for handling arsenical books were primarily based on Tedone and Grayburn's (2020) research. While infrequent handling of arsenical books is generally considered to be "low risk" from a health and safety standpoint, long-term exposure can lead to serious, long-term health consequences and "institutions may need to act with an abundance of caution because of issues surrounding legal liability" (Tedone and Grayburn, 2020, 110).

2. Tables and supports used during the examination of arsenical books should be wiped down to protect others who might use the space.

Vermeulen et al. (2023) recently conducted a study at Northwestern University Libraries to uncover books in their collection that contained arsenic. They discovered that items located near the arsenic-containing books also contained elevated levels of arsenic. While Special Collections has no current plans to test neighbouring items, it is crucial to remain mindful of the potential health and safety risks.

3. All books positively identified as containing arsenic and newly suspected items should be placed in appropriately labelled 100% polyethene zipper bags or CoLibri wrappers.

The library has taken necessary measures to ensure the safety of users and the preservation of the collection by enclosing books that contain arsenic on the cover, spine, and endpapers with CoLibri book covers. The use of clear and transparent polyethylene material allows for safe handling and opening of the books, and 100% polyethylene is a good long-term storage material. However, it is noteworthy that the covers are ineffective for books where arsenic has been identified on the fore-edge. It is also important to note that digital surrogates of books that contain arsenic have not yet been created, but the library recognizes the potential of digitizing the collection as a future project that will reduce the need to handle these books.

4. Arsenical books should be stored separately from the rest of the collection and relocated to a designated section within the library known as the "Hazardous Area." This section is part of the library's call number system and serves as an alert system for staff and library users regarding the potential hazards associated with these items.

It is imperative to house all arsenical items together in one location to ensure the library is well-prepared for emergency disaster response and recovery. By knowing

the precise location of arsenical titles, library staff can effectively identify health hazards for emergency responders, thus enabling the use of appropriate personal protective equipment (PPE).

5. The electronic catalogue record for each book should be updated with a local note, visible to anyone searching the database, identifying the item as containing arsenical emerald green.

Currently, there is no cataloging standard for adding health and safety information about each title in this system or in machine-readable cataloging (MARC) in the ExLibris Alma library management system used by Queen's. Therefore, the 590 field for "notes of local interest" (OCLC 2024) was used to describe the component and location of the arsenical green pigment:

590    ##\$aPaper cover colourant contains arsenic emerald green \$9local

The benefit of using the 590 fields is that they are searchable in Alma/Primo and are displayed in the Primo record, as noted in figure 10.

| Details          |   |
|------------------|---|
| Title            | Sir Brook Fossbrooke.   |
| Author/Creator   | <a href="#">Lever, Charles, 1806-1872 author</a> >  |
| Publication Date | MDCCLXX 1870  |
| Subject          | <a href="#">Arsenic -- Scotland -- 19th century</a> >   |
| Genre            | Arsenic -- Scotland -- 19th century   |
| Description      | By Charles Lever.<br>The last 7 pages are advertisements  |
| Identifier       | OCLC : (OCoLC)933113611   |
| Local note       | Paper cover colourant contains arsenic emerald green  |
| Series           | <a href="#">Blackwood's standard novels</a> ><br><a href="#">Blackwood's standard novels.</a> > |
| Publisher        | Edinburgh, William Blackwood and sons   |
| Edition          | New edition.  |
| Format           | [4], 503, [1], 7, [1] pages ; 18 cm.  |
| Source           | Library Catalog   |

**FIGURE 10** The detailed record for *Sir Brook Fossbrooke* displayed in Alma/Primo. Note that the "local note" details outline the composition and location of the arsenical emerald green component.

Additionally, an action note was included in the 583 MARC field, identifying the item as having tested positive for copper and arsenic through XRF analysis. The information in this field is not displayed in the public catalogue record.

6. If an item requires disposal, the established procedures as outlined by the University Environmental Health and Safety (EH&S) Department shall be

followed. Specifically, the "Hazardous Waste Disposal Procedures" document (2022) shall be referenced and adhered to, ensuring proper and safe disposal of the item.

It is crucial that books containing arsenic are disposed of according to the established procedures as outlined to ensure the safety of library staff, patrons and the environment. As stated earlier, arsenic poses serious health risks if mishandled or improperly disposed of. Proper disposal methods help mitigate the spread of arsenic contamination and ensure compliance with regulatory requirements, safeguarding the well-being of all those interacting with library collections.

## **Project Benefits and Challenges**

It must be noted that this project could not have happened without the collaboration of three key areas on the Queen's campus, the Library, the Department of Art History and Art Conservation, and the Master of Art Conservation program (MAC). Partnership with the Queen's Department of Art Conservation allowed access to the program's portable XRF to conduct the analysis. Queen's offers the only MAC program in Canada, and students specialize in conservation science. On several occasions, we were able to host students and faculty from the program in the lab to be active participants in the study. Both pXRF and Raman technologies are common scientific equipment that are multidisciplinary in use. As such, there are likely opportunities for many academic libraries to collaborate with their local science faculty to access pXRF and Raman equipment on campus since it is implausible for an academic library in Canada to own its own analytical equipment (i.e. pXRF or Raman).

In contrast, working on this project presented several challenges. One significant issue was the time-consuming nature of visually searching through the stacks to identify potential green candidates for testing. This task could be particularly daunting for understaffed libraries or archives, where resources are already stretched thin. Additionally, the problem of arsenic in book materials is frequently viewed as a niche concern, leading to difficulties in prioritizing this work amid other pressing responsibilities. The presence of arsenic may seem improbable or exaggerated to those unfamiliar with historical practices. Educating stakeholders about health risks further requires translating complex scientific information into accessible terms and demonstrating the risks of toxic pigments. Finally, overcoming the tendency to view this research as merely a curiosity involves emphasizing the broader implications for public health and safety. It is crucial that the work is seen as important to reduce any health risks associated with handling books that contain arsenic and that it is an

ongoing task. Our goal, through advocacy and collaboration, is to move it beyond a scholarly pursuit to a way to address a recognized public health concern.

## Conclusion

The 19th century brought tremendous change in the bookbinding industry. An increasingly literate public sought inexpensive reading material, and technological changes enabled publishers to meet the public demand. In addition, three critical inventions during this time, the introduction of book cloth, case bindings, and the arming press, allowed for the creation of identical or publishers' bindings.

Books, however, are very much connected to the culture and society in which they are created and produced. Books and their *objectness* cannot be understood in isolation, removed from the cultures and societies in which they were produced. Bookbindings, by their very definition, are constrictive. Their objective is to contain the text block and limit the amount of dust and debris allowed in, protecting the words and information contained within. Nevertheless, the information that bindings convey is boundless. As objects, they address more comprehensive questions relating to the culture in which they were created and used, the audience for which these cultural commodities were intended, and who was using them.

This relationship is evident in their connection to the use of arsenic in common household goods during the 19th century. During this time, there was a focus on the home and decorating it according to one's taste (Bartrip 1994). Colour was also important, and arsenic, or copper acetoarsenite, was used by manufacturers to colour fabric and paper into a brilliant shade of green. Although arsenic was well known to be hazardous to one's health, and despite pleas by scientists and doctors to stop using the toxic compound in common household goods, the use of arsenic persisted throughout the century.

Unlike wallpaper and clothing, books published during this time are available today in special and circulating library collections. However, until recently, the hazards to those who handle these artifacts were not fully understood. While XRF remains a reliable means of testing for arsenic in books, it may not always be accessible. In such cases, a visual assessment using a color swatch bookmark can be useful in comparing green hues that may suggest the presence of arsenic. Another valuable tool is the Poison Book Database (2023), which provides information on known toxic books and their features. By cross-referencing this database of book titles already known to contain arsenic, librarians can identify books in their own collections.



After the testing of approximately 150 items in the W.D. Jordan Collections and the positive identification of 28 items containing arsenic, it became clear that arsenical books in library collections are not an uncommon occurrence. As a result of the findings, changes were made at Queen's University Library to improve safe handling and long-term storage. It is hoped that the selection, identification, and testing methods used in this study will help other public and private library collections reduce the risk of handling and accessing these artifacts.

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## Appendix I

### *Summary of Book Titles at Queen's University Library that Tested Positive for High Levels of Arsenic and Copper Using XRF Analysis*

|   | OCLC #    | Call Number              | Title  | Date | Author          | Location        |
|---|-----------|--------------------------|--|------|-----------------|-----------------|
| 1 | 932843990 | QK91 .S7 1797 v.1 (pt.1) | <i>Caroli a Linne Species Plantarum, Vol. 1, Pt. 1</i> | 1797 | von Linné, Carl | edge decoration |
| 2 | 932843990 | QK91 .S7 1797 v.1 (pt.2) | <i>Caroli a Linne Species Plantarum, Vol. 1, Pt. 2</i> | 1797 | von Linné, Carl | edge decoration |
| 3 | 932843990 | QK91 .S7 1797 v.2 (pt.1) | <i>Caroli a Linne Species Plantarum, Vol. 2, Pt. 1</i> | 1799 | von Linné, Carl | edge decoration |
| 4 | 932843990 | QK91 .S7 1797 v.2 (pt.2) | <i>Caroli a Linne Species Plantarum, Vol. 2, Pt. 2</i> | 1799 | von Linné, Carl | edge decoration |
| 5 | 932843990 | QK91 .S7 1797 v.3 (pt.1) | <i>Caroli a Linne Species Plantarum, Vol. 3, Pt. 1</i> | 1800 | von Linné, Carl | edge decoration |
| 6 | 932843990 | QK91 .S7 1797 v.3 (pt.2) | <i>Caroli a Linne Species Plantarum, Vol. 3, Pt. 2</i> | 1800 | von Linné, Carl | edge decoration |
| 7 | 932843990 | QK91 .S7 1797 v.3 (pt.3) | <i>Caroli a Linne Species Plantarum, Vol. 3, Pt. 3</i> | 1800 | von Linné, Carl | edge decoration |
| 8 | 932843990 | QK91 .S7 1797 v.4 (pt.1) | <i>Caroli a Linne Species Plantarum, Vol. 4, Pt. 1</i> | 1805 | von Linné, Carl | edge decoration |
| 9 | 932843990 | QK91 .S7 1797 v.4 (pt.2) | <i>Caroli a Linne Species Plantarum, Vol. 4, Pt. 2</i> | 1805 | von Linné, Carl | edge decoration |

|    |           |                        |   |         |                               |                           |
|----|-----------|------------------------|---|---------|-------------------------------|---------------------------|
| 10 | 932843990 | QK91 .S7 1797 v.5      | <i>Caroli a Linne Species Plantarum, Vol. 5</i>   | 1810    | von Linné, Carl               | edge decoration           |
| 11 | 933165169 | JN2501 .L3 Vol. 1      | <i>Constitutions de la Nation Francaise, Vol. 1</i>   | 1819    | Lanjuinais, Jean-Dennis       | pesticide application     |
| 12 | 933165169 | JN2501 .L3 Vol.2       | <i>Constitutions de la Nation Francaise, Vol. 2</i>   | 1819    | Lanjuinais, Jean-Dennis       | pesticide application     |
| 13 | 932843990 | QK91 .S7 1797 v.6      | <i>Caroli a Linne Species Plantarum, Vol. 6</i>   | 1824    | von Linné, Carl               | edge decoration           |
| 14 | 932986955 | Mini JA55 .P6 1830     | <i>Politisches Taschenbuch fur das Jahr 1830</i>  | 1830    |                               | edge decoration           |
| 15 | 932938091 | PQ4338 .M26 1838t      | <i>Un Antico Manscritto</i>   | 1838    | Manetti, Giannozzo            | endpapers                 |
| 16 |           | Child PZ5 no.1324      | <i>Simple Stories, for the Amusement and Instruction of Youth</i>   | 1842(?) | MacDonald, W.R.               | paper cover               |
| 17 | 933304405 | Q54 .A894t             | <i>Atti Della Reale Accademia Delle Scienze, Sezione Della Societa Reale Borbonica, Volume V, Part II</i> | 1844    | Reale Accademia Delle Scienze | endpapers                 |
| 18 | 2128751   | LP E123 .C215          | <i>Histoire de la Découverte et de la Conquête de l'Amérique</i>  | 1845    | Campe, Joachim Heinrich       | decorative paint on cover |
| 19 | 933106872 | DA980 .M2 1854         | <i>Hand-Book to Galway, Connemara, and the Irish Highlands</i>  | 1854    |                               | bookcloth                 |
| 20 | 933177973 | PQ1165 .A428 1857t     | <i>Album Poetique des Jeunes Personnes</i>  | 1857    | Tastu, Amable Voiart          | decorative paint on cover |
| 21 | 932839261 | PR4728 .G8 A6 1857     | <i>Holland Tide</i>   | 1857    | Griffin, Gerald               | bookcloth                 |
| 22 | 976990603 | PR4728 .G8 Z63 1857t   | <i>The Life of Gerald Griffin</i>   | 1857    | Griffin, Daniel               | bookcloth                 |
| 23 |           | currently uncatalogued | <i>Les Saints Lieux: Pèlerinage à Jérusalem, Vol. 1</i>   | 1858    | Mislin, Jacques               | decorative paint on cover |
| 24 |           | currently uncatalogued | <i>Les Saints Lieux: Pèlerinage à Jérusalem, Vol. 2</i>   | 1858    | Mislin, Jacques               | decorative paint on cover |
| 25 |           | currently uncatalogued | <i>Les Saints Lieux: Pèlerinage à Jérusalem, Vol. 3</i>   | 1858    | Mislin, Jacques               | decorative paint on cover |

|    |           |                  |  |      |                  |                           |
|----|-----------|------------------|--|------|------------------|---------------------------|
| 26 | 10785275  | PQ2311 .J2 S9    | <i>Les Symphonies de l'Hiver</i>                             | 1858 | Janin, Jules     | decorative paint on cover |
| 27 | 635963229 | QK378 .O8        | <i>Plants of the Holy Land with Their Fruits and Flowers</i> | 1861 | Osborn, Henry S. | bookcloth                 |
| 28 | 933113611 | PR4884 .S55 1870 | <i>Sir Brook Fossbrooke</i>                                  | 1870 | Lever, Charles   | paper cover               |



## Appendix 2

### *Identifying Arsenical Books in Library Collections: A Quick Reference Guide*

Arsenic was commonly used in the manufacture of household goods during the 19th century, including wallpaper, clothing, and bookcloth. Bright green pigments from the Victorian era often indicate the presence of arsenic.

Please use these guidelines to identify items that may contain arsenic. Arsenic has also been found in paper bindings, endpapers, decorative cover embellishments, and fore-edge colourants.

- Publication date between approximately 1800 and 1900.
- Green colour like the examples below and colour swatch.
- Books that match in colour and fall within the date range should be bagged and sent to W.D. Jordan Library.
- Wear nitrile gloves when handling material suspected of containing arsenic. Wash your hands well with soap and water after any contact.



FIGURE 11 Arsenical green fore-edge.

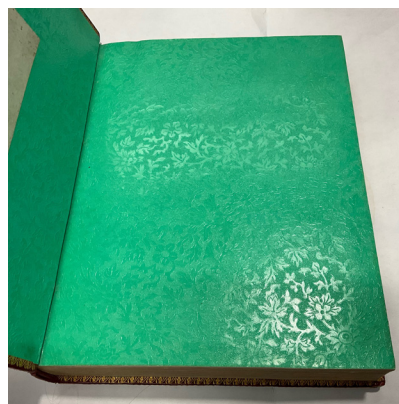


FIGURE 12 Arsenical green endpapers.



FIGURE 13 Arsenical green bookcloth.

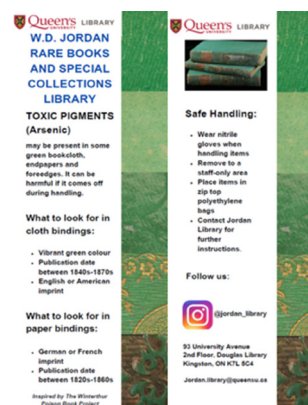


FIGURE 14 Colour swatch bookmark.