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Removal of stains caused by mercuric chloride treatments from herbarium sheet labels

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Abstract

Treatment of herbarium specimens with colorless mercuric chloride solutions was in the past a fairly common practice in botany collections. Over time the mercuric chloride on the sheets may undergo a series of reactions that result in gray-black stains that can completely obscure the data on specimen labels. A method has been developed using a modification of Lugol's iodine (a solution of iodine and potassium iodide in water) that removes the stains to reveal the printed and manuscript notations on the labels. Modifications include preparation of the Lugol's iodine using deionized water (pH 6.8–7.2), dilution of the solution to 20% of original strength using deionized water, and extensive rinsing of the labels with 99% ethanol or deionized water, extracted with blotters. The work must be carried out in a fume hood and used blotters must be treated as hazardous waste.

Keywords

botany collections, herbarium sheet labels, Lugol's iodine, mercuric chloride, mercury vapor, specimen labels, stains from mercury compounds, stain removal

Figure 1. Example of herbarium sheet and label with mercury salt stains. US North Pacific Exploring Expedition under Commanders Ringgold and Rodgers, 1853–56, US National Herbarium.

Introduction

While the precise origin of the use of mercury salts as treatments for botanical specimens is not clear, the use of a "corrosive sublimate" ($HgCl_2$, mercuric chloride) solution to dip nuts and seeds was noted in the 18th century (Forster 1771), and a mid-19th-century publication suggested that mercuric chloride would preserve vegetable substances (Babington 1843). The use of mercuric chloride solutions was reported at Kew Gardens as late as 1982 (Clark 1986), and the authors can attest to its continued use at herbaria in developing countries. Certainly over the past century alone, treatments with colorless solutions of mercuric chloride in water or alcohol are likely to have been applied to control biodeterioration by insects and microorganisms on hundreds of thousands of herbarium sheets in collections world-wide (Hawks and Von Endt 1990).

Unfortunately, over time the mercuric chloride residues from these treatments can undergo reactions that result in the formation of gray-black stains on the herbarium papers. The authors have observed that vascular plant specimens are rarely, if ever, stained by mercury treatments, while the mounting sheets and labels for the specimens are often blackened, and labels have been rendered illegible by the darkening (See Fig. 1). Analysis has shown that the stains contain HgS (metacinnabar, a cubic mercuric sulfide) and possibly 2HgO.HgS, a mercury oxide/sulfide compound (Sirois and Helwig 1996). Unreacted mercuric chloride may also be present on the papers (Sirois 1998).

The staining of specimen labels to the point of illegibility greatly threatens the utility of the specimens for scientific research. Consequently, several methods to remove the stains were explored by the authors.

Methods and materials

Non-invasive methods

As might be expected, efforts to read the label texts using dichroic filters, long- and short-wave ultraviolet radiation, and transmitted light all were unsuccessful. The metal salts reacted in the same way as the ink notations on the labels in various lighting situations.

Because gloves become stained from handling herbarium sheets that are stained by mercury salts, efforts to remove the stains by mechanical means were also explored by the authors. Some gray-black material could be removed from the labels by a gentle lifting motion with a soft brush, but the impact on text legibility was negligible. The use of various eraser-type cleaners was considered ill-advised

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because these might contain sulfur, which could exacerbate the conversion of unreacted mercuric chloride to dark compounds.

Water cleaning

The mercury compounds involved are not appreciably soluble in water or organic solvents, and tend to require strong acids or alkalis for solubility (Weast 1987); however, attempts were made to remove the stains with water on cotton tipped swabs. The technique was scarcely more effective than the use of dry swabs and did not remove enough of the stains to improve the legibility of labels.

Cleaning with a chelating agent

There are a great number of organomercury compounds, testimony to the ease with which mercury, and particularly, mercuric chloride, will bond chemically with organic substrates (Cotton and Wilkerson 1988). Thus, removal of the mercury stains was likely to be effected by the use of a chelating agent. A sodium salt of 2, 3,-dimercapto-1-propane sulfonic acid, which is used medicinally to chelate mercury from human tissues in instances of mercury poisoning was tested to see if it could remove the stains. While it worked slightly better than water, it also removed inks (including carbon-based inks) rendering it useless as an agent to clean labels.

Standard iodine solutions

Because iodine is known to react with mercury, and iodine solutions have been used to decolorize tissues stained with mercury salts (British Museum (Natural History) 1906), the authors experimented with various concentrations (0.1N, 0.05N, 0.025N) of a volumetric standard iodine solution (iodine, potassium iodide, hydrochloric acid–used to increase the solubility of the iodine, and water). At all concentrations, the solution removed the gray-black stains, leaving behind a yellow stain that could be partially removed by rinsing with distilled water. The yellow stains and the presence of the acid in the solution did not recommend it for cleaning paper substrates, particularly labels that would continue to remain on the herbarium sheets after the cleaning. Reportedly, iodine solutions in alcohol are especially effective in removing dark precipitates from materials fixed in mercuric chloride solutions, but the pH of the alcohol/iodine solutions is 2.9 (Speranza et al. 1987), which was considered to be unacceptable for use on paper.

Lugol's iodine

Lugol's iodine is a water-based oxidizing agent that does not contain an acid and is used to remove excess mercuric chloride fixatives from tissue preparations (Hine 1981). A fresh solution of the reagent was prepared using 0.5g iodine, 1.0g potassium iodine, and 50ml distilled water. Then 2.0ml of this solution were diluted in 10ml of distilled water and both the dilute and undiluted solutions were used in attempts to remove the mercury stains from a section of herbarium sheet. The stained area of the sheet was placed on a glass microscope slide, the liquids were applied directly to the stains with a pipette (the droplets remain in place; they do not disperse into the paper) and then blotted with pH-neutral, acid-free blotting paper. The procedure was repeated until the stain was removed, then the area was rinsed with distilled water to remove the yellow residue, and dried between clean blotters. While the technique worked well to remove the mercury stains, there was some formation of red spots in the formerly stained areas. The red spots were readily removed by rinsing with absolute alcohol (99% ethanol), suggesting that these are HgI_2 (mercuric iodide). Inks were undamaged by the treatment.

Because the pH of distilled water can be acidic (the pH of the dilute Lugol's iodine in distilled water was 6.1), experiments were conducted after preparing the reagent with deionized water from a reverse osmosis process. This water and the resulting solutions had pHs ranging from 6.8 to 7.2, as measured with a Hach

electronic pH meter, and maintained this range over several weeks. This pH range is compatible with that of standard herbarium papers, and will be slightly alkaline towards old papers with either acquired or inherent acidity.

In subsequent experiments the technique was refined to the following:

1. Mix a stock solution of 0.5g iodine, 1.0g potassium iodide, 50ml deionized (pH near neutral) water.
2. Dilute 2.0ml of the solution with 10ml deionized water (higher concentrations are no more efficient, and lower concentration do not work as well).
3. Mechanically lift the stained area of the label away from the herbarium sheet using a scalpel or bone folder (in most instances the old adhesive will give way readily). It is never wise to completely separate a specimen label from a sheet if this can be avoided.
4. Insert a piece of Silicone Coated Polyester Film® between the label and the sheet.
5. If no damage to the label will result, place a piece of unbuffered blotting paper between the Silicone Coated Polyester Film® and the specimen label. If this is not possible, insert the blotter under the herbarium sheet, on top of a glass substrate.
6. Place the reagent on the stains by dropping from a pipette.
7. Allow reagent to sit on the stain for up to one minute, then blot with unbuffered blotting paper topped with a glass microscope slide and weighted. Blue/gray-black deposits will form on the blotting paper.
8. Repeat the additions of reagent and the blotting until most of the stain is removed (it is not necessary to remove all of the stain to permit the text to be legible, and the label paper will appear lighter when dry).
9. Rinse the area by applying deionized water from a pipette, or if the label media are insoluble in ethanol, rinse with 99% ethanol. Blot between rinses.
10. Remove the silicone-coated polyester film and any blotting paper between the label and the film. Dry by placing the sheet and label on a blotter on a glass plate, topping with a blotter and another glass plate, and adding weights. Change the blotters as necessary until the paper is dry.

The process will require about one hour. In our tests the procedure did not damage inks, did not remove color from colored labels, and did not do significant damage to the surface of the label paper, although under magnification, it could be seen that the treatment had roughened the surface of the paper slightly. The labels generally re-adhere to the sheet during the final drying process. If not, reattach the labels with a suitable adhesive, such as methyl cellulose.

Safety precautions

The old name for mercuric chloride, "corrosive sublimate" highlights an important property of the salt. It sublimes at ambient temperatures. While there has been an erroneous belief that the sublimation occurred rapidly and that after a year the salts were no longer effective biocides (Spencer 1963), in fact the generation of mercury vapor from treated specimens can and does persist over time. In one study, concentrations of mercury vapor as high as 400μg/m^3 were recorded in cabinets of specimens treated over 30 years earlier (Briggs et al. 1983). In tests by the authors using a Jerome 431-X G old Film Mercury Vapor Analyzer in the US National Herbarium at the Smithsonian Institution, it was found that specimens treated with mercuric chloride in the early 1840s, now heavily stained, were still volatilizing mercury vapor.

Consequently, it is prudent to take precautions when handling herbarium sheets believed to have been treated with mercury salts. In the cleaning process described above, the work was carried out under local exhaust ventilation (fume hood). All of the small pieces of blotting paper used to extract the stains or in the rinsing process were placed in a fully labeled glass container inside the hood, then later disposed of as hazardous waste. Polyethylene gloves are recommended for handling mercury-contaminated materials (Lab Safety Supply 1998).

Figure 2. Herbarium sheet stained by mercury salts, with partially cleaned pale blue label. US Exploring Expedition under the command of Charles Wilkes, 1838–42, US National Herbarium.

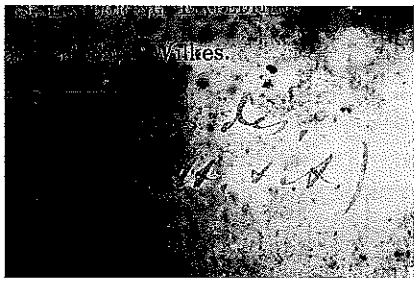

Figure 3. Detail of label shown in Figure 2, partially cleaned using modification of Lugol's iodine.

Conclusions

Because the process described above is time-consuming and involves extensive handling of toxic material, it is not recommended as a routine practice to remove stains from herbarium sheets or labels. Rather, this is viewed as means to salvage important data that would otherwise be lost to science. It poses some risk to the herbarium sheet and label, as well as to the conservator or collection staff person who undertakes the work. Complete removal of the label from the sheet would speed the process, but is not recommended unless there are very careful controls to ensure that the label eventually will be re-attached to the appropriate sheet (i.e., batch processing of numerous detached labels may not be feasible).

After nearly a year, there has been no reappearance of the stains on a historically important label that was partially cleaned for this project (See Figs. 2, 3). It seems unlikely that all of the mercury salts were removed by the treatment or were permanently altered to colorless compounds. Therefore it would be prudent to photograph the data immediately after a label has dried, in order to be certain that the information will remain available even if the label should discolor again over time.

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References

Babington C. 1843. Report of the Committee for the Preservation of Animal and Vegetable Substances. In: Report of the 12th meeting of the British Association for the Advancement of Science held at Manchester June 1842. London: John Murray: 40–41.

Briggs D, Sell P, Block M, I'Ons R. 1983. Mercury vapour: A health hazard in herbaria. New Phytologist 94:453–457.

British Museum (Natural History). 1906. Handbook of instructions for collectors. 3d ed. London: Hazell, Watson and Viney.

Clark S. 1986. Preservation of herbarium specimens: An archive conservator's approach. Taxon 35: 675–682.

Cotton F and Wilkerson G. 1988. Advanced inorganic chemistry. 5th ed. New York: John Wiley and Sons.

Forster J. 1771. A catalog of the animals of North America ... to which are added short directions for collecting, preserving and transporting all kinds of natural history curiosities. London: B White.

Hawks C and Von Endt D. 1990. Mercury and mercury compounds in natural history collections: An annotated bibliography. Natural history conservation (5): 4–19.

Hine I. 1981. Block staining of mammalian tissues with hematoxylin and eosin. Stain Technology 56: 119–123.

Lab Safety Supply. 1998. Working with mercury. EZ Facts Safety Info Document No. 235. Janesville, Wisconsin: Lab Safety Supply.

Sirois J. 1998. Analysis of mercury compounds on herbarium sheet test specimens. Analytical Research Laboratory Report No. 3708. Ottawa: Canadian Conservation Institute.

Sirois J and Helwig K. 1996. Analysis of darkened areas on mounting papers used in historical herbarium specimens. Analytical Research Laboratory Report No. 3599. Ottawa: Canadian Conservation Institute.

Snyder S, Vigo T. 1974. Removal of mercury from aqueous solutions by N-(2-aminoethyl)aminodeoxycellulose cotton. Environmental Science and Technology 8(10): 944–946.

Spencer G. 1963. Control of pests in insect and herbarium cabinets. Proceedings of the Entomological Society of British Columbia 60: 23–26.

Speranza V, Skinner R, Boylston E, Fromowitz F. 1987. A disadvantage of alcoholic iodine solutions for removal of mercury pigment from tissue sections. Journal of Histotechnology 10:253–255.

Weast R, ed. 1987. Handbook of chemistry and physics. Boca Raton, Florida: CRC Press.

Materials

Iodine (99.99+%) and 0.1N Iodine Volumetric Standard Solution (ACS reagent grade iodine, potassium iodide and hydrochloric acid in ASTM reagent grade water), Aldrich Chemical Co, Inc., Division of Sigma-Aldrich Inc., 101 West St Paul Avenue, Milwaukee, WI 53233 USA, Tel (414) 273-3850,Website http://www.sigald.sial.com.

Potassium iodide (99+% ACS reagent), Fisher Scientific, 585 Alpha Drive, Pittsburgh, PA 15238 USA, Tel (800) 766-7000, Fax (800) 926-1166, Website http://www.fisher1.com.

Ethanol (ethyl alcohol, USP, 200 proof), Warner-Graham Company, DSP-MD 43, Cockeysville, MD, 21030 USA.

2,3, -dimercapto-1-propane sulfonic acid sodium salt (medicinal chelating agent for mercury), Sigma Chemical Company, PO Box 14508, St Louis, MO 63178-9916 USA, Tel (800) 521-8956,Website http://www.sigald.sial.com.

Reliance® blotting paper, #4-13-01-37 (pH neutral, unbuffered blotting paper), Frank Parsons Paper, Company, 2270 Beaver Road, Landover, MD 20785 USA, Tel (301)386-4700.

Hach 43800-00 Portable pH Meter with Hach One® Combination Electrode (pH meter), Hach Company, PO Box 389, Loveland, CO 80539 USA, Tel (800) 227-4224, Fax (303) 669-2932.

Silicone Coated Polyester Film® (1.5mil Mylar D® film coated on both sides with silicone), Conservation Support Systems, PO Box 91746, Santa Barbara, CA 93190-1746 USA, Tel (800) 482-6299, Fax (805) 682-2064.

Jerome 431-X Gold Film Mercury Vapor Analyzer, Arizona Instrument, Phoenix AZ 85040-1941, USA, Tel (800) 235-3360 (in USA), Fax (602) 470-1888, email azi@netzone.com.

Polyethylene gloves, Lab Safety Supply, PO Box 1368, Janesville, WI 53547-1368 USA, Tel (800) 356-0783 or (608) 754-7160 (international), Fax (800) 543-9910 or (608) 754-1806 (international), Website http://www.labsafety.com.

Methyl cellulose (synthetic cellulose powder), University Products, Inc., 517 Main Street, PO Box 101, Holyoke, MA 01041-0101, Tel (800) 638-1912, Fax (800) 532-9281, Website http://www.universityproducts.com.