ARSENIC IN TAXIDERMY COLLECTIONS: HISTORY, DETECTION, AND MANAGEMENT

Fernando Marte,[1,2] **Amandine Péquignot,**[1,3] **and David W. Von Endt**[1]

[1]*Smithsonian Center for Materials Research and Education, 4210 Silver Hill Road, Suitland, Maryland 20746, USA*

[2]*Taller TAREA, Escuela de Humanidades, Universidad Nacional de San Martín, 1784 Benito Q. Martín, Ciudad de Buenos Aires, 1296, Argentina*

[3]*Centre de Recherche sur la Conservation des Documents Graphiques, FRE 2743, Muséum National d'Histoire Naturelle, 36 rue Geoffroy Saint Hilaire CP 21, 75005 Paris, France*

Abstract.—An historical review of taxidermy treatments shows that arsenic has been used in the preparation and conservation of specimens from the 18th century until recent times. Two spot tests for arsenic detection have been tested and compared: the Weber's test and a kit developed by Macherey-Nagel. Stuffed birds from the Muséum National d'Histoire Naturelle, Paris and standard arsenical solutions were spot tested and results compared with those using Inductively Coupled Plasma Spectrometry (ICPMS). The spot tests compared well to the results using expensive equipment, are freely available, inexpensive and provide an adequate level of detection down to 20 ppm. All specimens should be monitored even those that test negative first time round. Institutions should be responsible for monitoring levels of arsenic in collections, use appropriate protection when handling all specimens and regularly update health and safety records.

Introduction

Pesticides have been used in museum collections for a long time. Many of these compounds are toxic to human beings and can be a potential danger to individuals who are in contact with these collections. In taxidermy, arsenic was one of the principal substances used in the preparation of skins. In different taxidermy handbooks, arsenic, realgar, and orpiment were used in preservative recipes. Taxidermists usually use arsenic as arsenical soap, which was applied to the inner side of the specimen skin to preserve it from bio-deterioration and insect attack.

Today curators, conservators, scientists and technicians have to deal with the hazardous effects of this element. Different analytical techniques such as XRF, ICPMS, and SEM-EDS can be used to detect arsenic in collections. Most museums do not have the access to this technology, but this is not always necessary as spot tests provide an alternative method to detect the presence of arsenic.

This study aims to compare two different arsenic spot test methods, provide further information concerning their limits of detection and recommendations for arsenic detection in taxidermy collections.

Arsenic in Taxidermy: A Long History

By the middle of the 18th century, collectors of natural history specimens were experiencing problems with preserving their collections and at that time produced a vast amount of literature on the subject. They used the generic term *Preservative* to describe the products used for skin tanning and conserving. Boitard (1881) defined it as ''an antiseptic substance that possesses [several] conservative properties.'' Specimens were often dried and preserved with salt, herbs, alum, spices, or tobacco. These ''recipes'' were only effective for a short period of time causing

the specimens to smell unpleasant. Naturalists then decided to try new techniques for preserving bird and mammal skins. They substituted techniques that had been used in dried collections for a new group of very strong and effective poisons, for example, mercuric chloride dissolved in water, corrosive sublimate, or arsenic.

Arsenic compounds have been used as therapeutic agents since the 5th century BC, when arsenic sulfide was recommended for the treatment of ulcerated abscesses. Arsenic was isolated in ca. 1250 by the German physicist and alchemist Albertus Magnus (ca. 1200–1280). While heating arsenic sulfide (As_2S_3) with soap he sublimated arsenic. From the eighteenth and up until the nineteenth centuries, arsenic was prescribed for disorders, such as tuberculosis, rheumatism and syphilis (Anonymous 1752, Bescherelle 1856).

Arsenic is mainly present in two forms: organic (when associated with carbon and hydrogen) and inorganic (combined with chlorine and sulfur), the inorganic form being more toxic. Its principal ores are mispickel (FeAsS), realgar (As_2S_2), orpiment (As_2S_3), and loellingite ($FeAs_2$). When exposed to humid air, arsenic tarnishes with trioxide of diarsenic (As_2O_3), a very toxic powder often used as rat poison. Realgar has long been used in medicine, and alchemists experimented with it until the Middle Ages. This is a very fragile red mineral that with extended exposure to light causes the crystals to decompose to a yellow-orange powder (arsenolite and orpiment).

In different taxidermy handbooks, arsenic, realgar, and orpiment were used in preservative recipes. As early as the 18th century, taxidermists employed a mixture of realgar and orpiment dissolved in water with lime or *vert-de-gris* (copper acetate) for the conservation of skins. Another technique used involved the covering of skins with a terebenthine and camphor varnish. At the moment of the mounting, the interiors were then covered with a mixture of arsenic and aloe. During the stuffing of the skin, a dry mixture of corrosive sublimate ($HgCl_2$), arsenic, alum, camphor, and occasionally cinnamon (to give it a good smell), was used. Apart from being used as a tanning agent, arsenic was also employed as an insecticide. Its smell was considered better than that of sulfur, which caused specimens to change from red to yellow, darkened blue specimens and occasionally caused them to burn. In taxidermy, arsenic is better known for the preservative arsenical soap, invented by the French Jean-Baptiste Bécoeur (1718–1777). During his lifetime, Bécoeur kept the composition of his miraculous product a secret and it was not revealed until 1800 (Dufresne 1800). The preservative was composed of camphor, arsenic oxide, carbonate of potash, soap and lime powder. This composition has been fairly constant through the centuries (Péquignot 2002). At the end of the 19th century, arsenical soap was indexed in the *Codex Medicamentarius* (Anonymous 1866), and was under strict regulation in France, under the *Loi sur la vente des substances vénéneuses du 19 juillet 1845,* and under the *Ordonnance royale portant Réglement sur la vente des substances vénéneuses du 29 octobre 1846.* The formula was arsenic (320 g), carbonate of potash (120 g), distilled water (320 g), soap (320 g), lime (40 g) and camphor (10 g). At the time, arsenical soap was a real advance in the art of taxidermy and at the end of 19th century many handbook authors recognized Bécoeur as the inventor and an important player in the history of taxidermy. His arsenical soap was employed until the 1980s in different museums around the world (Hawks and Williams 1986,

McCann 1995, Knapp 2000). Because of its toxicity (Le Dimet and Jullien 2002), the use of arsenic is now prohibited in the museum community.

DETECT TO PROTECT

The history of taxidermy shows us that the vast majority of stuffed animals found in museum collections may have been prepared with arsenic. This does not only cover ''ancient specimens'' as arsenic has been used in more recent times (Hawks and Williams 1986, Knapp 2000). Knowing which specimens are contaminated is vital so that preventative measures can be taken to protect the health of individuals in contact with collections. This includes taxidermists, researchers, and even the general public as some of these objects are still exhibited.

First it is necessary to visually inspect the specimens for the presence of characteristic white arsenic dust. These powdery or crystalline deposits are normally found at the base of hairs and feathers, around eyes, in or at the base of ears, around mouths or bills, and on foot pads. In addition to this examination, some knowledge of the object's history will be helpful to determine when, and by whom it was collected and prepared, and if arsenic was used in that period. Then it is necessary to test specimens for arsenic, as the absence of white powder does not mean the absence of arsenic. For that purpose there are several available techniques. Sirois and Sansoucy (2001) presented different techniques available to detect arsenic in collections. Because many museums may not have the opportunity to use high-technology (XRF, ICPMS or SEM-EDS), but they still need to detect the presence of arsenic, spot tests are a good alternative. We decided to test and to compare three different methods on a skin sample prepared by arsenic: the Weber's test, a kit developed by Macherey-Nagel sold commercially, and the ICPMS (Inductively Coupled Plasma Mass Spectrometry). We prepared and tested a set of standard solutions, as well as a set of samples of arsenic tanned skin from the Muséum National d'Histoire Naturelle, Paris.

Weber's test is commonly used in American museums (see for example Found and Helwig 1995, Hawks and Williams 1986, Sirois and Taylor 1989). This test was devised by Stephen Weber (University of Pittsburg) and is based on the Gutzeit method developed in Germany in the 1920s (Vogel 1965). In this process, the arsenic compounds react with hydrogen produced from the reaction between zinc and acid (hydrochloric or sulfuric). The hydrogen reduces the arsenic compounds to arsine (AsH_3), a poisonous gas. The arsine is then exposed to a paper treated with mercuric chloride solution to produce a yellow to brown color, depending on the concentration of arsenic. The limit of sensitivity commonly accepted is 20 μg per drop of standard arsenic (Hawks and Williams 1986, Sirois and Taylor 1989). This limit was chosen as it is the ''background'' level of arsenic in soil and water that is the result of leaching from natural sources and from two centuries of applying arsenic in agriculture. It is assumed that when the tests are carried out on water and soil, at least 20 μg will be present per drop of sample after dilution. This background level defines the detection limit when using the tests for these purposes. The detection limit is therefore estimated to be around 400 ppm.

The *Arsenic Paper Test* kit manufactured by the Macherey-Nagel Corporation (USA) and recommended by Odegaard et al. (2000) and Odegaard and Sadongei (2005) is a modification of the Weber's test. Arsenic present in the sample is

reduced to arsine gas, which turns the test white paper (containing 1.9% mercuric (II) bromide) lemon yellow to brown according to the concentration. The detection limit stated by the company, is 0.1 ppm of arsenic for a 5 ml sample (20 ppm) and a box of 200 strips (Art-Nr. 907 62) costs approximately $25 at the time of writing. The procedure involves careful physical removal of some crystalline powder residues or rolling fine cotton swabs dampened with distilled water over the specimen (Fig. 1). The cotton swab is then broken off and placed in an Erlenmeyer flask with 25 ml of distilled water. After an hour, 5 ml of this solution is placed in a test tube and 10 drops of concentrated chlorydric acid and around 0.5 g of zinc powder are added. The test paper is quickly introduced and the tube closed with a laboratory wrapping film (Parafilm™) cap. After 30 minutes the paper test can be read.

We also tested the sensitivity and accuracy of these two procedures against results from the Perkin Elmer Elan 6000 Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) at the Smithsonian Center for Materials Research and Education (USA). The ICP-MS was connected to a cross flow nebulizer sample introduction device. The parameters of the ICP-MS were optimized to ensure a stable signal with a maximum intensity over the full range of masses of the elements and to minimize oxides and double ionized species formation ($XO+/X+$ and $X++/X+ < 3$ %). The nebulizer gas flow, lens voltage, detector analog stage voltage and detector pulse stage voltage were adjusted to achieve this. A dual detector calibration was applied to match the analog and pulse detector stages and was required to measure major, minor and trace elements at the same time.

We tested both paper methods on the specimen samples and then on the arsenic solutions. We used the ICP-MS to determine arsenic concentrations for the specimen samples and arsenic solutions. Skin and feathers from the samples, were tested in different areas of the specimen. They were prepared by acid digestion in 70% nitric acid (HNO_3) since chloride reacts with argon interfering with the readings. Digestion was conducted in a microwave at a pressure of 30b, a temperature of 260°C, for 15 min at 400W and then 30 min at 800W. ICP-MS analyses revealed an arsenic concentration of 935 ppb (0.935 mg/L) for skin samples and 173 ppb (0.173 mg/L) for feather samples. For the Weber's Test and the Arsenic Test Paper we removed some crystalline residues by rolling fine cotton swabs dampened with distilled water and followed each test procedure. Both tests gave a positive result with a stronger signal for the Weber's test than for the Arsenic Test Paper.

The results show that the Weber's test and the arsenic paper test are positive at 200 ppm concentration of arsenic, as there is a strong black/brown coloration. The reaction still clearly appears at 100 ppm for both tests, and two tests still react at 20 ppm. At 7 ppm, no reaction was observed in the Weber's Test and it is very difficult to read a positive answer in the Arsenic Paper Test (Fig. 2). We can observe positive results for Weber's test below the 400 ppm sensitivity previously estimated (but results should be taken with caution when concentrations are lower than 400 ppm). Results for the Arsenic Paper Test are consistent with the 20 ppm limit stated by the supplier. Both tests are very sensitive and are suitable for arsenic detection. From the practical point of view, the Weber's test gives a very quick answer but it requires previous training in the handling of chemical compounds. The Arsenic Paper Test is easier to use but the process

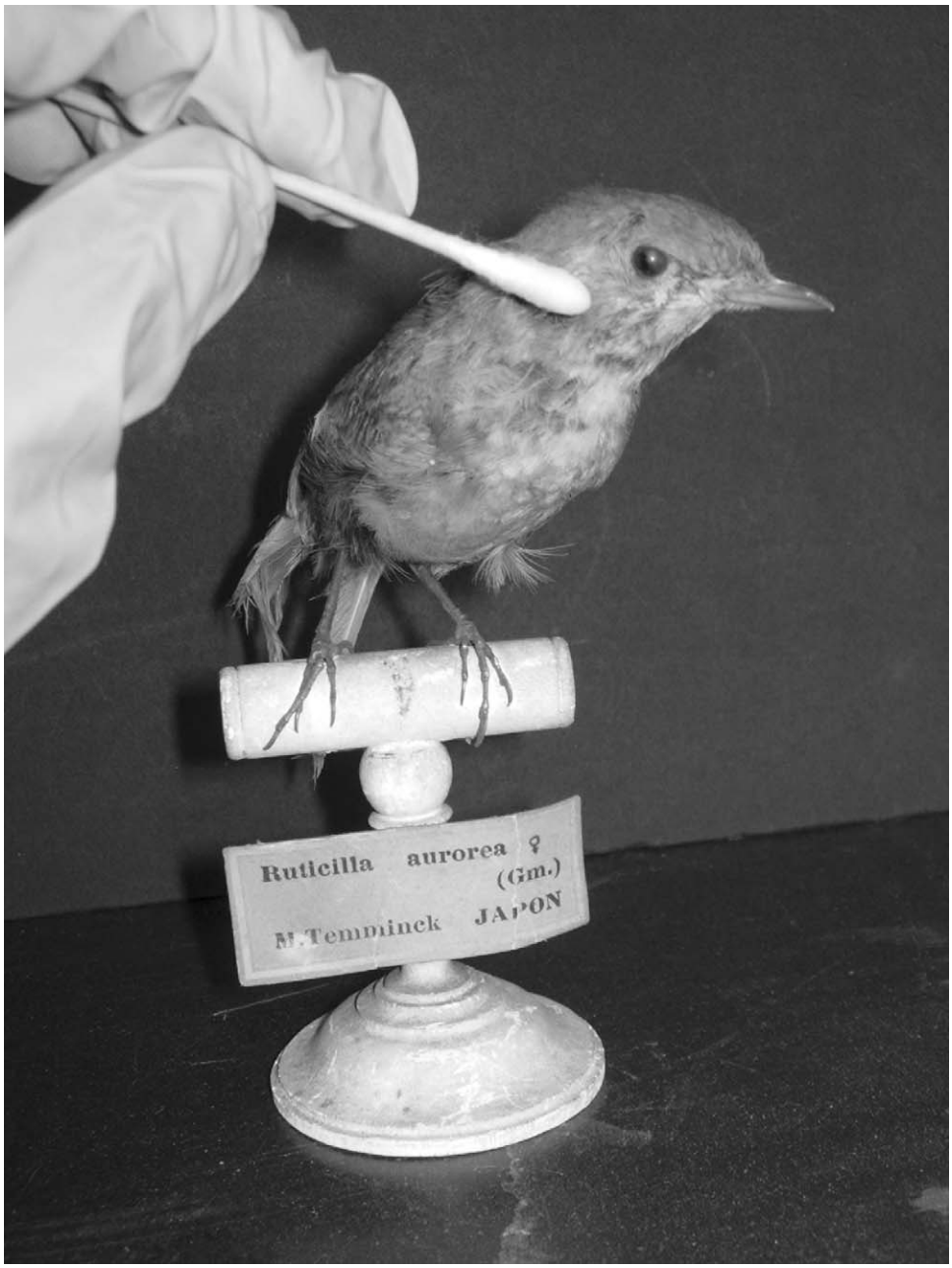

Figure 1. Rolling a cotton swab on a bird specimen for an Arsenic Spot Test at the Muséum National d'Histoire Naturelle, Paris.

takes longer, as 30 minutes are needed before readings can be taken. Spots tests can be use to determine the presence of arsenic in taxidermy specimens when proper and careful sampling is practiced. It is essential to test several areas as negative results can be obtained from some parts of contaminated specimens.

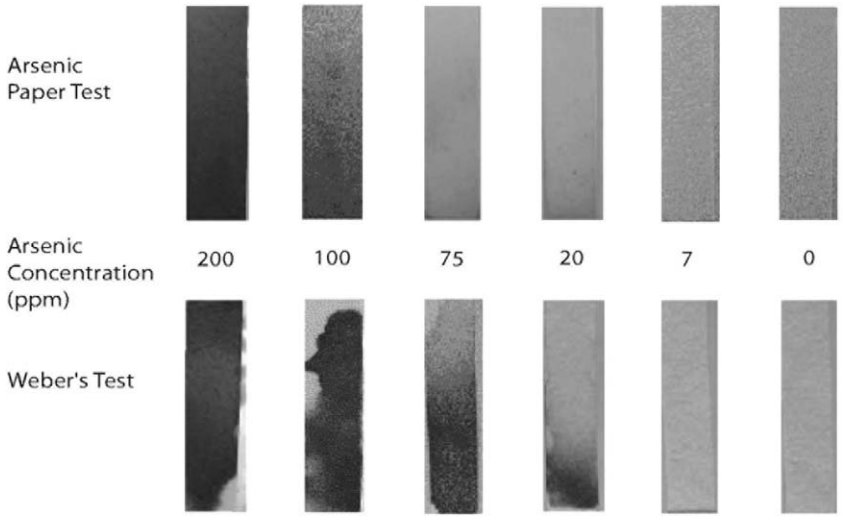

Figure 2. Results from Weber's Test and the Arsenic Paper Test on the solutions at different arsenic concentrations (7, 20, 75, 100 and 200 ppm).

Arsenic Management

Arsenic when present in museum collections requires an appropriate level of management, as does management of the information associated with the contaminated specimens. It is important for institutions to develop a protocol for handling arsenic contaminated objects that covers not just employees but also researchers and visitors. Specimens known, or suspected to contain arsenic should never be handled without appropriate protection. Nitrile gloves and a protective smock or apron, as well as a respirator, are necessary in dealing with these objects. These supplies should be disposed of in an appropriate way similar to other hazardous materials. Specimens testing positive for arsenic must have ''Arsenic contaminated'' clearly visible on their labels (Knapp 2000). This information must also be added to the museum paper and/or computer catalog. It should be noted that objects that tested negative might still contain arsenic (Palmer 2001). These objects should be inspected and tested every two to three years, as arsenic may migrate from the interior of the specimen. Each test result, whether positive or negative, must be recorded in the specimen's computer and/or paper catalog entry. These specimens should be stored separately whenever possible. Objects that are contaminated with arsenic should not be exhibited without appropriate conditions and/or decontamination to reduce the risk of exposure. A High-Efficiency Particulate Air (HEPA) vacuum could be used to absorb at least part of the arsenic powder on the specimen (Knapp 2000). This method may have restricted application in taxidermy because arsenic or arsenical soap was usually applied as a paste on the inner side of the specimen skin.

Conclusions

Spot tests such as the Weber's test and the Macherey-Nagel paper are freely available and inexpensive methods that can identify arsenic in taxidermy collections and help to manage this contamination problem. These two spot tests were

successfully calibrated against ICP-MS results on arsenic standard solutions and bird specimens. The spot test methods are sensitive enough to detect even background levels of arsenic. However, specimens that give negative results should be re-tested every two to three years. It is the responsibility of museums to identify those objects that are contaminated and to provide a safe environment to their staff and visitors.

Acknowledgments

Christophe Gottini and Frantz Jullien, taxidermists at the Muséum National d'Histoire Naturelle de Paris are thanked for providing skin samples. Dr Laure Dussubieux helped with the ICPMS analysis. Catharine Hawks also provided advice.

Literature Cited

Anonymous. 1752. *Dictionnaire de Trévoux—Dictionnaire Universel Français et Latin, Contenant la Signification et la Définition de l'Une et l'Autre Langue, avec des Remarques d'Érudition et de la Critique.* La Compagnie des libraires associés, Paris, France, 5 volumes.

Anonymous. 1866. Substances Vénéneuses. Pp. 701–708 in *Codex Medicamentarius, Pharmacopée Française Rédigé par l'Ordre du Gouvernement.* Baillère, Paris, France. 784 pp.

Boitard, P. 1881. *Manuel Complet du Naturaliste Préparateur, Taxidermie—Préparations des Piéces Anatomiques Contenant l'Art d'Empailler et de Conserver les Animaux Vertébrés et Invertébrés; de Préparer les Végétaux et les Minéraux; de Faire les Préparations Anatomiques; de Conserver les Cadavres Temporairement ou Définitivement, Nouvelle Édition Refondue et Complétée par M. P. Maigne.* Roret, Paris, France. 420 pp.

Beschrelle, L.N. 1856. *Dictionnaire National ou Dictionnaire Universel de la langue française, tome I.* Garnier Freres, Libraires-Editeurs, Paris, France. 1319 pp.

Dufresne, L. 1800. Sur l'Art de la Taxidermie, considéré par rapport aux Oiseaux, c'est-à-dire sur l'art de dépouiller, de droguer, de conserver et de monter les Peaux d'Oiseaux. Pp. 439–462 in An VIII [1800]. *Traité Élémentaire et Complet d'Ornithologie ou Histoire Naturelle des Oiseaux.* (F.M. Daudin, ed.). Chez l'auteur, Paris, France, I. 474 pp.

Found, C. and K. Helwig. 1995. The reliability of spot tests for the detection of arsenic and mercury in natural history collections: A case study. Collection Forum 11(1):6–15.

Hawks, C.A. and S. Williams. 1986. Arsenic in natural history collections. Leather Conservation News 2(2):1–4.

Knapp, A.M. 2000. Arsenic Health and Safety Update. Conserve O Gram Washington, DC: National Park Service September (2/3):4.

Le Dimet, S. and F. Jullien. 2002. Arsenic et vieux spécimens. La Lettre de l'OCIM. Special Issue Hors série Taxidermie décembre 105–107.

McCann, M. 1995. Arsenic and other preservatives in museum specimens. Art Hazards News 18(2): 1–2.

Odegaard, N., S. Carrol, and W.S. Zimmt. 2000. *Material Characterization Tests for Objects of Art and Archaeology.* Archetype Publications, London, England. 230 pp.

Odegaard, N. and A. Sadongei. 2005. *Old Poissons, New Problems, A Museum Resource for Managing Contaminated Cultural Material.* AltaMira Press, New York, USA. 126 pp.

Palmer, P.T. 2001. A review of analytical methods for the determination of Mercury, Arsenic, and Pesticide residues on Museum objects. Collection Forum 16(1–2):25–41.

Péquignot A. 2002. *Histoire de la Taxidermie en France de 1729–1928, Etude des Facteurs de ses Évolutions Techniques et Conceptuelles, et ses Relations à la Mise en Exposition du Spécimen Naturalisé.* Thèse de Doctorat, Muséum National d'Histoire Naturelle, Paris, France. 390 pp.

Sirois, J.P. and G. Sansoucy. 2001. Analysis of Museum Objects for hazardous pesticides residues: A guide to techniques. Collection Forum 17(1–2):49–66.

Sirois, J.P. and J. Taylor. 1989. The determination of arsenic and mercury in natural history specimens using radioisotope X-ray energy spectrometry and scanning electron microscopy. Pp. 124–136 *Proceedings of the 14th Annual IIC-CG Conference May 27–30, 1988, Toronto, Ontario, Canada.*

(J.G. Wellheiser, ed.). The Toronto Area, Conservation Group of The International Institute for Conservation of Historic and Artistic Works, Canadian Group 179 pp.

Vogel, A.E. 1965. *A Textbook of Macro and Semi-micro Qualitative Inorganic Analysis,* 4th ed. Longmans, London, England. 663 pp.