Blessing and curse – biocides: application, analysis, evaluation

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Editors
Andrea Lang and Judith Zimmer

Design
Ilka Linz

Layout and Reprography
Bettina Aigner, Berlin

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Fur hat for non-commissioned officers and troops,
Queen Victoria of Prussia’s 2nd Hussar Bodyguard Regiment
Nr. 2, pre-1914 © DHM, Berlin

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Regine Falkenberg

Do we have a chemistry problem?

Curator of Material Culture II: Civilian Costume and Textiles, Religious Objects and Badges

That's the question hundreds of people ask themselves every day when they are unable to get along with one another. It's one that we also often ask at the German Historical Museum (DHM), because some of the objects in our collection can cause different kinds of chemistry problems – those that involve health.

The DHM is an esteemed, institutionalized location for depositing and exhibiting historical remains and evidence. Its collections lie at the root of all the work we do. Over the centuries, objects become imbued with historic memories, because they were part of life as it was lived during a particular epoch. Objects are authentic and concrete. Their materiality secures a kind of permanence, while their historical significance creates a passion to preserve. That's why we cannot simply avoid poisoned or toxic objects in our depot as we would disagreeable people. To the contrary, even more than other objects in our care, they require our full and undivided attention.

Since the end of the 1990s, systematic research – primarily in the DHM's textile collections – has shown that curators over the decades have used the current, tested methods of their time to preserve collections from climatic damage and/or destruction by animals. As early as the 1960s, woolen cloth was treated with an insecticide known as 'Eulan', and later stored in cupboards together with bags of naphthalene and moth-killing paper. The wood of the storage cabinets was in turn usually saturated with wood preservatives like Hylotox, which contains lindane and DDT. Based on the idea that 'more is better', protective measures were multiplied, along with the chemical reactions that the curators unknowingly set in motion. By the turn of the century, when restorers at the DHM discovered the first white crystallization stains on objects made with fur trim, it became clear that the various measures that had been undertaken would continue to have an impact on the collections for an indefinite period of time. When the museum's textiles collection took over about 1,500 civilian workers' garments from the museum's 'Militaria' department in the year 2002, it led to huge health issues among staff. By then, the problem we faced had dimensions. It had become clear that the biocides used – whatever they were – would not grow less toxic over time 'all on their own', nor would they simply 'evaporate'.

We initially shared those fears with the German Worker Compensation Board (VBG) and, in 2005, with the German Federal Accident Insurance Fund. An analysis carried out on air and dust samples at the DHM by the German Institute for Occupational Safety (BIGA) did not result in any spectacular findings. In the case of Eulan, however, there were no reference values or benchmarks available for comparison. To protect ourselves from the possibly harmful effects of chemical substances in general, DHM curators and restorers began wearing protective gear that included respirator masks, dust coats and protective gloves.

Because the possibilities for analysis have developed and improved very rapidly in the last few years, while also growing increasingly precise, staff[1] from the DHM's Collection and Restoration Departments decided to push for a research liaison with the Division for the Analysis of Artefacts and Cultural Assets at the German Federal Institute for Materials Research and Testing (BAM)[2].

The goal as formulated in the project proposal was to develop an efficient method economically for "Risk analysis in biocide-laden artefacts and cultural assets". Instead of examining an endless stream of individual samples, the project's aim was to create a non-destructive, reliable method for analyzing biocides at both quantitative and qualitative levels on site in museums. The two-phase project, which was carried out between 2009 and 2012, was financed by the German Federal Commissioner for Culture and Media. Its first results are now being made available to the wider public in this online publication.

Introduced at two workshops that took place in Berlin, the investigations and analyses revealed that toxic traces on and in tissue were not just due to verified insecticides present in the collections (Eulan, naphthalene, moth-killing paper, Hylotox). Toxic substances used in the manufacture of the items in question or possibly applied to it during its period of use are also at times present in amounts that can be hazardous to health. This result has increasingly drawn the focus of attention to the anthropogenic history of the objects. In the future, this data can be used to help verify an object's authenticity, and it opens new perspectives in terms of exhibition themes.

A museum that works with traditional artefacts and displays them in the public realm not only has to protect staff and visitors from the dangers of organic and inorganic toxins, but must also stick to certain guidelines when it comes to presentation. Objects made of contaminated textiles, for example, should not be presented in direct proximity to documents, since paper can filter out and absorb toxins from the environment. Constraints like this affect content in exhibition interdependences, which have to be well-planned in advance and at times explained to visitors. For this reason, the results from the scientific analysis of an object also provide interesting information for the historians, art historians and cultural studies experts who will be working with it in an exhibit.

Textile restorers at the DHM have grown more relaxed about working on their historic charges, and are happy that "people no longer smile when they see us dressed up like astronauts in our protective gear." Thanks to research and education measures, the presence of possibly dangerous chemical compounds in historic objects has now become an idea that has gained broad acceptance. And with the huge numbers of objects made of plastics in the 21st century, coping with toxins in restoration and preservation is certain to be a field with a future.

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1. Thanks especially to efforts on the part of DHM Head Curator and Deputy President Dr. Dieter Vorsteher-Seiler (retired in 2014), Head of Restoration Martina Homolka, textile restorers Judith Zimmer and Andrea Lang, and Administrative Director Bernd Burmeister.
2. Thanks to Dr. Oliver Hahn and Sonja Krug for their commitment in this collaboration.

Helene Tello

Handle with Care – Toxic Residues of Preventive Conservation in Museum Collections

History of conservation, items of art and culture, insect pests, pesticides, application processes

Introduction

The history of using pesticides[1] composed of organochlorine or heavy metal compounds to prevent infestation with insect pests and conserve and protect museum collections of artistic and cultural objects goes back to the time of the Enlightenment. The following article is dedicated to answering the question of how it came to be that pesticides were used extensively in numerous collections in the past. It also addresses which non-toxic measures can be applied as preventives to avert infestation in the present day.

General preventive measures against insect pests

Careful consideration of other methods is in principle a must before pesticides are used on museum collections to ward off insect pests and prevent possible damaging infestations. The properties of the storage buildings – including their fixtures, cabinets and shelves – are initial deciding factors for storing collection objects. Ideally, depots, storage rooms and exhibition rooms should already have features that deter the entry of insects, birds and rodents. Furthermore, a nearly windowless building with a consistent interior climate is desirable for storing collections well. This example of a historical photograph showing feathered items from the Ethnological Museum in Berlin, formerly the Royal Ethnological Museum, makes it clear that pest control in accordance with the Integrated Pest Management (IPM) of today certainly could not have been carried out in the completely overfilled cabinet (Fig. 1). By contrast, clearly arranged storage of collection items in metal cabinets equipped with legs, which do not rest on solid bases or panels are advantageous. Floor areas can easily be accessed for cleaning and monitored with respect to insects that may be present (Fig. 2). Individual storage of collection items with the aim of preventive conservation serves to structurally stabilise the object, allow contact-free work on it and the possible detection of pests early on.

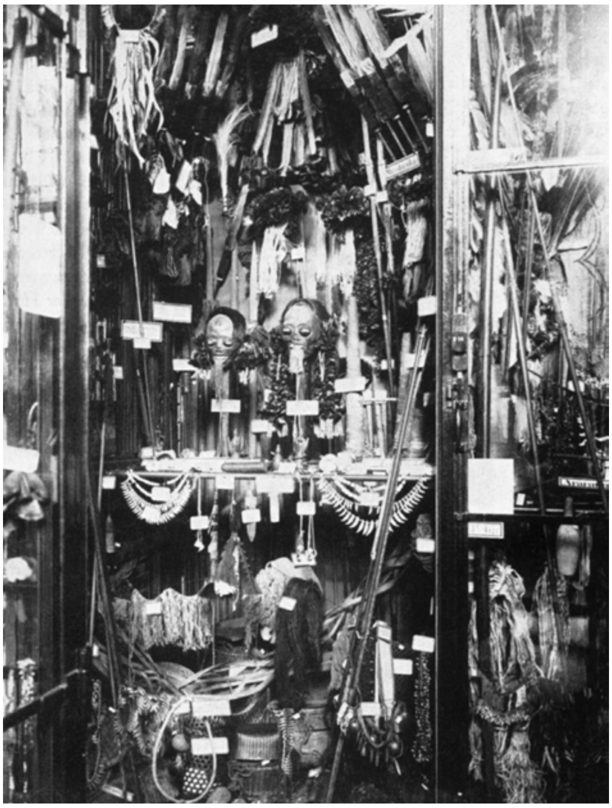

Fig. 1: Inside a specimen cabinet of the South American collections in the former Royal Ethnological Museum in Berlin.

© Ethnologisches Museum, Staatliche Museen zu Berlin-Preußischer Kulturbesitz

The Historic Use of Pesticides to Ward Off Insect Pests in Museum Collections

Since the start of the Enlightenment in the 18th century, a continually increasing number of museums of natural sciences contributed to the search for substances, methods and processes that could successfully be used to protect individual objects composed of organic material and comprehensive collections against pests. Furthermore, extensive collecting was taking place on a Europe-wide scale during the colonial period, meaning collections of objects composed of organic materials, natural history preparations and herbaria were growing dramatically. In contrast to structural and preventive conservation measures, the use of pesticides to combat insects, fungi and bacteria

Fig. 2: Inside the storage area of the Natural History Museum in New York.
© Helene Tello

in museum collections involved a direct intervention in the substance of objects and materials. Pesticides vary greatly in their composition with respect to their target organisms and application methods. Individual entries in acquisition files of Berlin's Ethnological Museum show that the use of pesticides on museum collection items, for example, was already taking place in the countries of origin in the 19th century. Beyond that, pesticides were also used at the museum to prevent pest infestation after the arrival of comprehensive collections.[2, 3] In 1888, the Royal Museums of Berlin, today the National Museums of Berlin, established the first scientific laboratory in the world dedicated to the conservation of antiquities under the leadership of Friedrich Rathgen (1862–1942). He directed the Rathgen Research Laboratory from 1888 to 1927 and in 1898 published the first, and 1924 an expanded, new edition, of his monograph "The Preservation of Antiquities" – in German *Die Konservierung von Alterthumsfunden, Handbücher der Königlichen Museen zu Berlin*.[4, 5] This manual was also available to staff at the former Royal Museum of Ethnology, whose first curator was Eduard Kraus (1847–1917). The book provided what was then state-of-the-art knowledge on fighting pest infestation of items made of organic materials (Table 1). Rathgen was searching for methods to remove insects en mass from bundles as they arrived at the Royal Museum of Ethnology and were added to collections rapidly growing as a result of purchases, gifts and major expeditions. Through his activities, the first fumigating facility was installed in the newly constructed storage building in Berlin-Dahlem in 1924. First they relied on carbon disulfide, then tetrachloroethylene, or perchloroethylene, which was known by its brand name, *illo-gas*. It was not until 2004 that Berlin's Ethnological Museum received modern nitrogen and freezing chambers, which made the further use of chemicals to fight off insect pests unnecessary. In other places, *Zyklon B*, which was used in the concentration camps in the Second World War, was still used from the 1950s to the 1960s to fumigate artworks and cultural objects. *Zyklon B* contains the effective ingredient prussic acid (hydrogen cyanide). It was applied to shredded cellulose poured directly out of metal cans. During this procedure, the prussic acid is released slowly from the cellulose in a controlled manner (Fig. 3).

A handbook providing "instructions for collecting, preserving and packaging of animals" (*Anleitung zum Sammeln, Konservieren und Verpacken von Tieren*) by August Bernhard Brauer[6] was published in 1907 for natural history museums. Brauer was a German zoologist and director of the Berlin Zoological Museum from 1906 to 1917. In a practice orientated manner, he describes with sophistication different processes for wet and dry preparation of specimens. He recommends splitting into pocket shapes the ears, lips and eyelids of mammals. Dry skins must be kept pliable with water and then daubed with arsenic soap on the inside surface. Arsenic soap or potassium arsenate should be spread over the inside of the skin of birds' heads and necks. Brauer also recommends particular care in treating the skin of the lower legs, upper arms and the base of the tail. Feathers covering the wings are to be raised for treatment. Arsenic soap is to be spread over the slit area under the wing where it meets the body. For birds with more robust legs, Brauer recommends the application to the skinned soles as well. And finally, arsenic soap is to be applied to the feet and beak. He does not advise, however, that unprepared bird skeletons be treated with arsenic, because it prevents or makes leaching more difficult later on. To prevent insect damage, Brauer recommends naphthalene or insecticide powder for reptiles and amphibians. As an alternative, however, they can be placed for a longer period in saline solution with alum. Formaldehyde can also be used for wet preparation. Yet Brauer notes that insects that have been treated in this way can become

Table 1: Recommended substances and chemicals against pests for organic materials provided by F. Rathgen 1898 and 1924.

Substances	Physical Properties	Procedures	Materials
arsenic-soap	solid		fur, fresh
benzene	gaseous	fumigation	grain, nuts, seeds, wood
benzine	gaseous	fumigation	grain, nuts, seeds, wood
camphor	solid	scattered	woolen tissues
carbon disulfide	gaseous	fumigation	fur, leather, horn, paper, papyrus, rope, bast
chloroformates	gaseous	fumigation	woolen tissues
crude benzene	gaseous	fumigation	grain, nuts, seeds, wood
crushed pepper	solid	scattered	feathers
crushed pepper mixed with powdry alum	solid, gaseous	scattered, fumigation	feathers
cyanoformates/-acetates	gaseous	fumigation	woolen tissues
Eulan solution	liquid	dipping	woolen tissues
Globol (PDB),	solid	scattered	woolen tissues
hydrocyanic acid	gaseous	fumigation	woolen tissues
kerosene	liquid	dropping, soaking	tusk
naphthalene	solid	scattered	feathers, hair, tissue, grain, nuts, seeds, wood
potassium arsenate, aqueous solution	liquid	dropping	grain, nuts, seeds, wood
sodium arsenate, aqueous solution	liquid		fur, old
mercury(II) chloride (sublimate), alcoholic solution	liquid	dipping	feathers, hair, tissue
mercury(II) chloride (sublimate), aqueous solution		spray	feathers
α-Tetralon (3,4-Dihydro-1(2H)-naphthalinon)	solid	scattered, fumigation	grain, nuts, seeds, wood
tetrachloromethane	gaseous	fumigation	grain, nuts, seeds, wood
Zapon or Zellon mixed with poppy-seed oil	liquid	dipping	grain, nuts, seeds, wood
dry heat: 60-70°C			fur, leather, grain, nuts, seeds, wood, woolen tissues

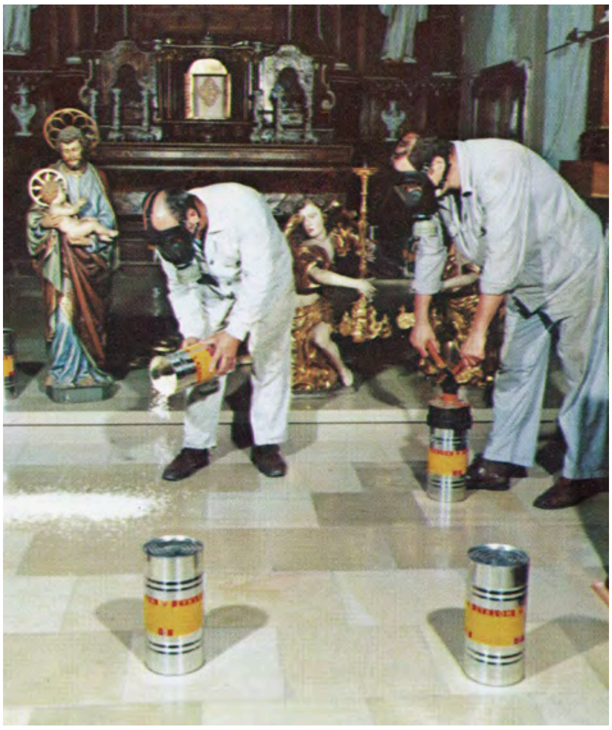

Fig. 3: Fumigation of a church with *Zyklon B*.
from: Riederer 1977, with the kind permission of Josef Riederer

Fig. 4: Staff members during the fumigation of mammal skins at the scientific bellows collection at the Natural History Museum of Berlin, circa 1930
© Kästner-Archive, Gothenburg, Sweden

brittle and fragile. As an alternative, he suggests placing sticks of potassium cyanide in the base of jars and pouring a fresh, viscous mixture of water and plaster over the specimens. Regular fumigation was also carried out at the Berlin Museum of Natural History in addition to the use of pesticides on wet and dry preparations (Fig. 4). The collections at the Ethnological Museum experienced a clear turning point in the use of pesticides between 1941 and 1958, so during and after the Second World War. Large parts of the collections were shipped westwards, to the art storage warehouse at Celle Palace. The Red Army of the former Soviet Union carried off other parts of the collections to Leningrad (now St. Petersburg) as the spoils of war. In the 1970s, these were then transported to the Grassi Museum in Leipzig. Intensive treatment of the collection items was carried out with different pesticides at each of the locations. In still divided Germany, these compounds frequently differed greatly from one another in their brand names, their composition and description of their ingredients. The economy of scarcity prevalent everywhere at that time hampered the target-orientated application of pesticides with respect to the organism they were aimed at, meaning, in other words, that products were often used for purposes for which they were not designated. As a result of the war, the Rathgen Research Laboratory remained closed for a long time after 1945. It was only reopened and resumed work under the direction of Josef Riederer in 1974. A monograph he published in 1977 in conjunction with the exhibition “Art and Chemistry” (*Kunst und Chemie*) at the former National Museums of West Berlin marks a further milestone in the science of conservation of museum collections.[7] The knowledge it contains about fighting pests was available to conservators at the time and documents the close cooperation between natural scientists on the one hand, and the chemistry industry on the other.

The Application Procedure for Pesticides

Fumigation to prevent pest infestation is just one of many types of application procedures. In addition, pesticides were sprayed, scattered and distributed, in the form of moth balls and moth paper. They were also injected, applied with a brush or through saturation or dipping. Fabric restorers have found bags with the label *Globol* among the fabrics stored at the warehouse of the *Germanisches National Museum*. Behind the brand name *Globol* is the effective ingredient 1,4-dichlorobenzene, formerly known as paradichlorobenzene (PCB). Ti*pp fix 82* with the ingredients bioallethrin (pyrethroid) and lindane (γ-hexachlorocyclohexane were used in the former East Germany. *Texyl* was also used there as a spray or in mechanical atomisers to prevent clothes moth infestations. Until 1988 *Texyl* contained the ingredients lindane and poly-

chlorinated camphene, and after that, lindane and permethrin. *Impra Hgf* is a wood preservative containing lindane and pentachlorophenol (PCP) that was made in the former West Germany and used, among other places, at the National Museums of West Berlin. Spraying with dichlorodiphenyltrichloroethane (DDT) with the help of a DDT sprayer was quite common in many households in the 1960s. The production and spread of DDT and its persistent effects can be seen even until this day. In the year 1965 alone, 30,000 tonnes of DDT were produced in West Germany. Until 1972 around 2 million tonnes of it was used around the globe to prevent the spread of malaria and typhus, in agriculture, forestry, as a structural wood preservative and in homes to prevent insect infestation. It was not until 1996 that global production of DDT fell to 5,000 tonnes. Residues of DDT have already been found in Swiss glacial lakes. Accelerated glacial melting caused by climate change has in the meantime released the toxins that had been stored in the ice over decades.[8]
Therefore, it is no surprise that DDT has already been detected in Antarctic ice.[9] Until the late 1990s, the compound camphor was spread in the Ethnological Museum in specimen cabinets to prevent insect infestation.

Finding concrete evidence of previous use of pesticides on items in the collection is occasionally like detective work. Written documents on file cards, entries in inventory books or direct clues on objects and preparations are rare finds. A label with the word “poison” on the cover of a specimen of seal gut from the National Museum of Natural History of the Smithsonian Institution in Washington, D.C., fails to reveal the compound applied or effective ingredient used (Fig. 5). GOLDBERG nevertheless found in the archives of the Smithsonian Institution in Washington, D.C., numerous indications of the use of arsenic, mercury (II) chloride, naphthalene and dipping in gasoline as well as regular fumigation of entire collections.[10]

Final Observation

Pesticides today pose a considerable problem to restoration and conservation because they are located in the matrix of the material of museum specimens and can cause some degree of irreversible damage both within and on the items. The saturation of an object

Fig. 5: Labelling of the cover of a seal gut specimen, dated 12 September 1884 from the collection of the Anthropological Department of the National Museum of Natural History, Smithsonian Institution.

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with a pesticide that was applied earlier is often dependent on the process used to apply it and the intensity of the application. Over the course of time, pesticides have been emitted from collection items, prepared specimens and herbaria and have concentrated themselves in the air and dust. Because they are non-water soluble as a rule, washing them out, including for example DDT out of fabrics, is not possible. The current efforts to remove the contaminants from objects left by preventive conservation are complex. Many approaches to pesticide decontamination are being pursued. With the help of thermal processes, vacuum desorption, solvent rinsing and extraction procedures using fluid or supercritical carbon dioxide, research is being done to find ways of minimising the threat pesticide emissions pose to people who have contact with these collection specimens.[11, 12]

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Birte Mull and Oliver Jann
Biocide emissions from materials in the air

Most organic biocides belong to the group of semi volatile organic compounds (SVOC). Classical biocides are e. g. lindane, pentachlorophenol (PCP) and dichlorodiphenyltrichloroethane (DDT), newly biocides are e. g. dichlofluanid, tebuconazole, and permethrin. During the 1950s and 1960s biocides were especially used in museums to protect exhibits[1] and are now mostly detectable in storage rooms due to their acute and preventive use in there[2]. In course of time it was determined that biocides both influence the human health negatively and cause damages on treated exhibits[3]. Various possibilities to analyze biocides and the influence of sink-effects on the analysis are presented in this article.

Possibilities for biocide analysis

Emission test chambers for biocide analysis

Emission test chambers are used to determine emission rates of semi volatile biocides, as it is also done for volatile organic compounds, according to DIN EN ISO 16000 9[4]. Very high sampling volumes (up to the m^3 range[5, 6]) are necessary due to their low volatility and these measurements are taking a lot of time (up to several months) because of sink effects. Further experiments were done in a micro chamber (Micro-Chamber/Thermal Extractor™, Markes International) rather than in 1 m^3- and 0.02 m^3-chambers[7, 8] to avoid long sampling times. The micro-chamber consists of six cells with a volume of 44 ml, which can be heated up to 120 °C[9]. A temperature increase from 23 °C to 80 °C (air flow through the chamber cells: 25–30 ml min 1; air change: 34 40 h 1; area specific air change rate: 1.7 2.0 m^3 m ^{2}h 1) results in a higher emission potential of biocides from treated materials. Consequently, the emission process is accelerated and results concerning the emission behaviour are obtained faster. The low chamber cell volume is a disadvantage, because most samples need to be destroyed for the measurements. Direct thermodesorption is a further analytical method where results concerning the sample composition and contamination are obtained faster but the samples have to be much smaller as for micro-chamber measurements[7]. To avoid contamination of the thermodesorption system it is further possible to extract small sample pieces to a downstream sorption tube (e. g. filled with Tenax® TA or quartz wool)[10].

Adsorbents for biocide analysis

Polyurethane foam (PUF) is an often used air sampling adsorbent to analyze biocides[6, 11]. New micro-chamber investigations indicate that a surface modified styrene divinylbenzene polymer (SDVB-polymer) (Phenomenex, Strata™ X, 200 mg) offers also good adsorption properties for biocides. Lindane, PCP, dichlofluanid, tolyfluanid, isodrin, permethrin and p,p’ DDT could successfully be analysed with the SDVB-polymer[12, 13].
Jann et al.[10] showed that Tenax® TA (poly-2,6-diphenyl-p-phenylenoxid) and glass wool can also be used as adsorbents but only for higher volatile biocides. These adsorbents are thermally desorbed before injection onto the gas chromatography column, whereas PUF and SDVB-polymer are liquidly desorbed, which worsens the sensitivity.

Analysis

A chronological separation of the compounds is done using a gas chromatograph (GC) and identification and quantification is done using a mass spectrometer (MS) as detector. Depending on the used adsorbent the samples are either liquidly or thermally injected onto the GC column.

Behavior of biocides

The low volatility and the connected emission time of biocides became obvious in an experiment by Horn et al.[14] running since 1994 in which dichlofluanid, tebuconazole and permethrin could still be detected in measurable amounts after approximately 3200 days (Figure 1). The emission rates of tebuconazole and permethrin are to be regarded as quasi steady.

Sink-effect

The sink-effect has an important role by analyzing semi volatile compounds, since it influences the results during the whole experiment[15-17]. Jann et al. performed experiments regarding the sink-effect with dichlofluanid, permethrin and tebuconazole in 0.02 m^3-chambers. Figure 2 shows the percental concentration decrease of dichlofluanid, permethrin and tebuconazole after removing a sample from the emission test chamber, which confirms the existence of sink-effects. The boiling point of dichlofluanid is the lowest of the three biocides; hence, it is the biocide with the highest volatility, which can be seen by the comparatively fast concentration decrease. Concentration values of typical volatile compounds (VOC like e. g. solvents) would have been decreased to amounts close to zero within less than an hour under the chosen conditions (instead of days as for the presented biocides).

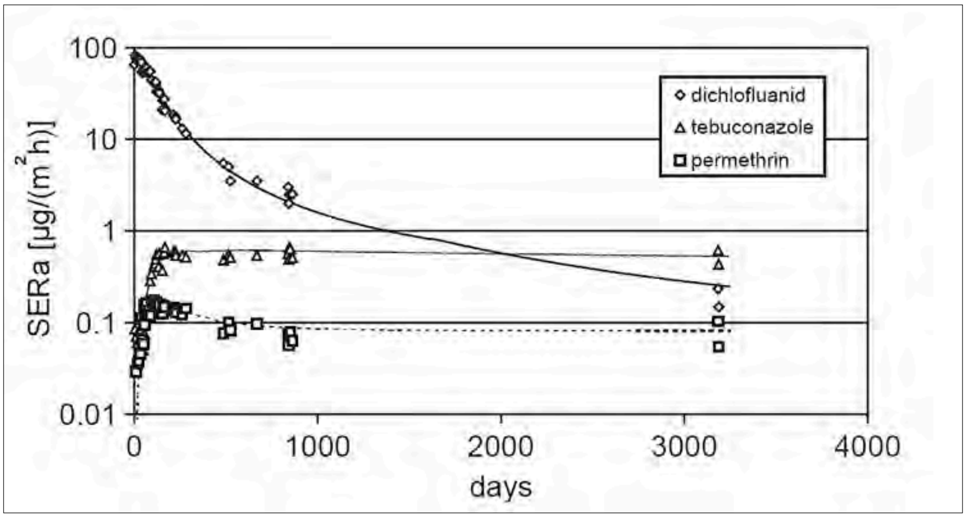

Fig. 1: Progress of the area specific emission rates (SERa) of dichlofluanid, tebuconazole and permethrin for a period of approximately 9 years.[14]

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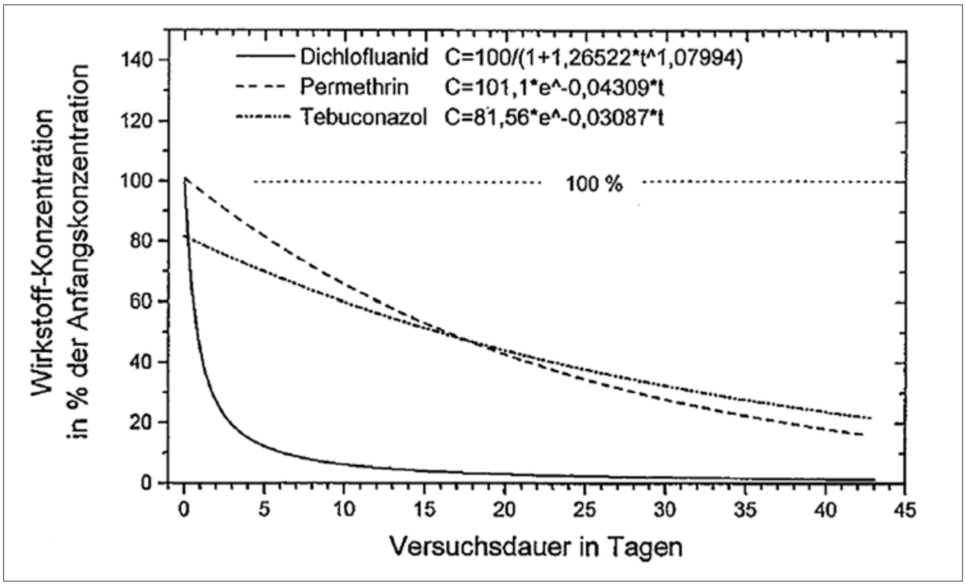

Fig. 2: Concentration progress (in %) of dichlofluanid, permethrin and tebuconazole.[10]

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Conclusion

The analysis of biocides in air can be performed successfully both with different adsorbents and in different emission test chambers. Sink- and memory-effects have, as above mentioned, important impacts on the measurable air concentrations and on secondary contaminations. The long emitting property of biocides was illustrated in the experiment lasting more than 3200 days. For that reason they can still be detected several years after their application indoors, mostly dust-bonded, and on the treated objects. Due to sink-effects and secondary contaminations it is even possible to detect them on non treated surfaces and objects. Hence, removing of the primary source might only reduce the air concentration minimally.

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Andrea Lang and Judith Zimmer
The long path to a measured result

A working report on the research project "The effects of historic pest control on textile collections at the German Historical Museum".

A three-year project sponsored by the German Historical Museum (DHM) and the German Federal Institute for Materials Research and Testing (BAM) gave staff at the museum the opportunity to widen their knowledge about current contamination levels in its textile collections. One of the primary goals of the research was to quantify potential dangers in order to better protect personnel and visitors.

Background

The DHM's textile collections for the most part originally came from collections kept in the historic *Zeughaus* (Armory) building. They included in particular flags, uniforms and military equipment made of materials like wool, leather, silk, fur or feathers. In addition, the inventory includes extensive collections of both civilian and military textiles inherited from the former Museum for German History (MfDG) as well as from the DHM. All in all, it covers a huge range of possible materials and combinations.

There was never any doubt that at least parts of the collection were contaminated, since many of the objects in question had been tagged with the label "Eulan" or "Eulan BLN 3%", and at times additionally labels bearing a particular date. Other indicators are found on old inventory cards, or have been communicated orally over time. Specific odors associated with the objects in question appear to confirm this.

Back in the mid-1990s, conservators first noticed crystalline exudations on uniforms, which in 1997 were identified by Dr. Achim Unger (Berlin State Museums) as the compound methoxychlor. Further examinations that took place in 2005[1], 2007[2] and 2008[3] confirmed the presence of the non-specific insecticides DDT, DDE, lindane, eulan and other methoxychlor compounds, and analyzed them.

The results of those examinations, our inadequate knowledge in relation to determining the actual contamination levels in the collection, a general sense of insecurity in handling the objects in it, and – most especially – concerns about the health of the staff


Fig. 2: Crystallized biocide on the jacket of an old uniform.
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Fig. 1: Eulan warning tag.
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Fig. 3: Crystallized biocide, detail from Fig. 2.
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involved were all motivating factors back in 2009 to launch the project we report on here.

Concerns

More than any other factor, what drove this project forward was the desire to protect the group of people who have contact with objects like these on a regular basis. The priority therefore initially focused on defining potential dangers. A further intention was to review the practicality of standard measuring methods for evaluating contamination in both quantitative and qualitative terms, as well as to develop such methods further.

A representative selection of objects needed to be measured at the depot on site. The project's stated goal was to develop a non-destructive method for testing, especially when it came to measuring organic compounds. Special attention was to be paid to contamination levels of objects and furnishings, as well as to air quality in depots and workspaces. Also of interest was possible damage to objects, and the interactions that might have occurred between individual objects and/or wooden storage cupboards and an object.

Another major concern for the staff at the DHM was to have digital access to all of the project data.

Preliminary considerations

Discussions during the collaboration focused initially on occupational safety issues, and later examined possible approaches to the measurements that needed to be taken from both the air and the objects. Based on the biocide evidence described above, the German Federal Accident Insurance Fund in 2008laid down the guidelines for occupational safety during the project. Since 2009, these measures have been reviewed and implemented within the project's framework. These have an impact in particular on the following areas:

→ information for staff
→ personal protective gear
→ identification of and disposal of contaminated storage cabinets and packing material
→ cleanup of depots
→ information for visitors to depots and representatives from borrowing institutions
→ courier delivery of contaminated objects.

Air measurements in rooms and cabinets were to be taken actively with the help of TENAX ® TA products, and subsequently evaluated via gas chromatography-mass spectrometry (GC-MS). Because we had to assume we were dealing with a number of volatile organic substances, sampling was to be carried out with different adsorption media. To obtain an approximation of the amounts of biocide involved, the project participants decided only to open some cabinets that had been closed for longer, pre-determined periods of time. In addition to the air measurements, investigators were to take samples from cabinets and swab samples from object surfaces.

In measurements involving objects, the investigators decided to employ X-ray fluorescence (XRF) spectroscopy to identify inorganic elements. In respect to suspected biocides, they initially chose to search for the marker elements mercury, arsenic, lead and chlorine. This approach was intended to provide a foundation for a planned second phase of the project that would involve measuring organic compounds. The investigators carried out extended discussions in advance on the relevance of exactly which different parameters should be allowed to influence results – in short, the qualification and especially the quantification of the raw data.

The investigators decided to measure each object at a representative number of points, meanwhile ensuring that different materials as well as different locales on the objects came under investigation. Each individual point was to be characterized exactly, using predetermined terms to describe material, color, surface texture, layer thickness and material combinations in layer structures.

At the same time that XRF spectroscopy measurements were carried out, the project planners foresaw testing with a UV-Vis[4] spectrometer, which produces spectrograms that could help identify dyes at individual test points. Before the measurements for organic substances commenced, we discussed the suitability of a range of methods for providing the information curators need. The starting point for these discussions was the stipulation that the methods used had to be non-destructive, which excluded the taking of physical samples or subjecting collection objects to mechanical tests such as crushing or squeezing them. Where suitable and allowed by the limits of XRF spectroscopy, the challenge was to take as many measurements as possible on site in the depots. Additionally, the investigators wanted to test out various methods for possible application, including GC-MS, Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy and emissions measurement in a desiccator. Raman spectroscopy initially appeared to be a promising approach, although it later proved to be unable to accomplish our goals.

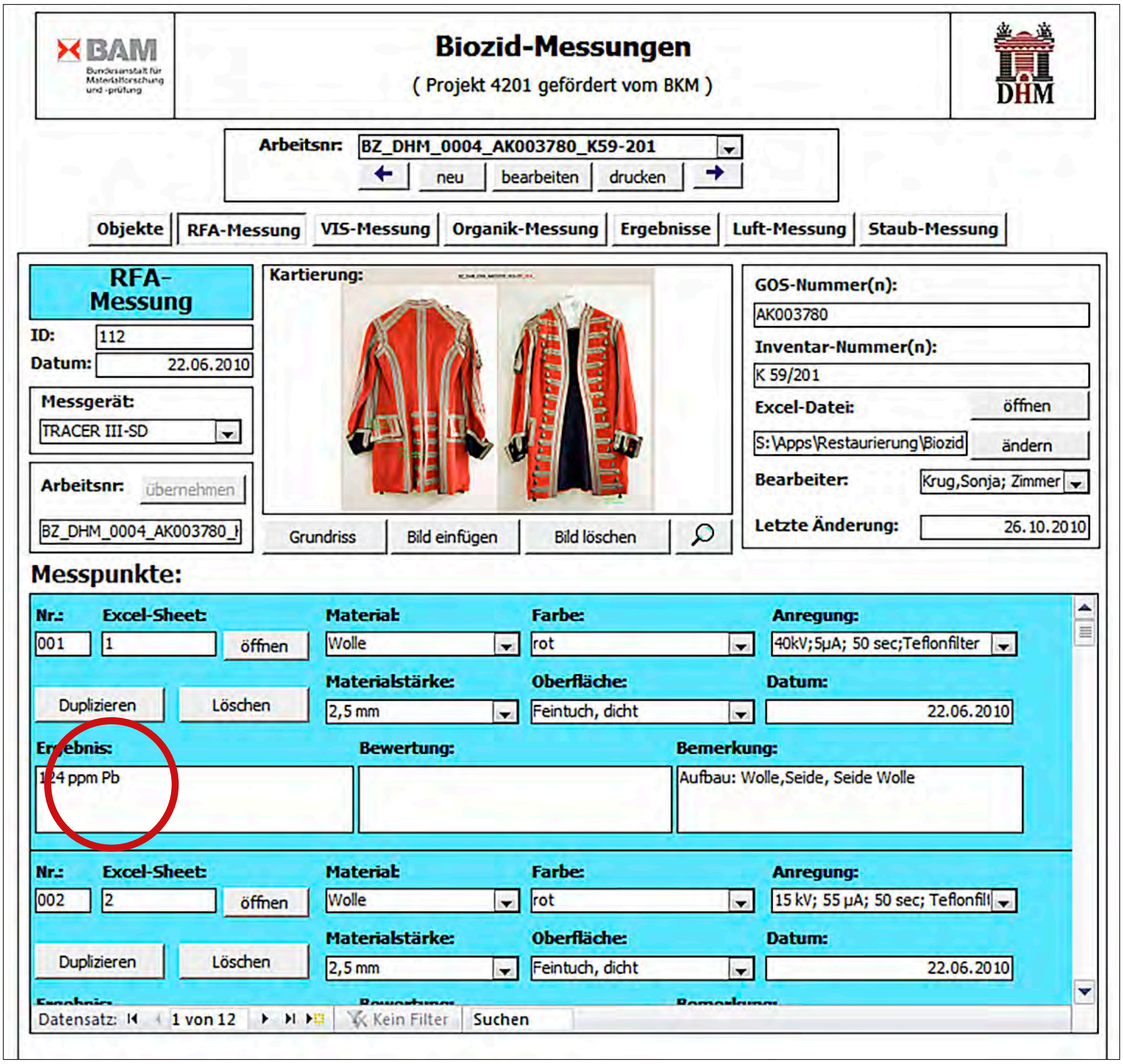
The investigators had to compromise in preliminary discussions, finally agreeing to measure far fewer objects than originally intended. Emissions from individual small-format objects such as head coverings and epaulettes were to be measured in the desiccator, while minimal samples from around ten other objects that exhibited high levels of chlorine were to taken for further GC-MS analysis.

We also decided that all details – including measurement data and protocols, photographs, point mapping, reports, spectra and evaluations – were to be compiled in a new project database that would be available to all project staff on the DHM's intranet.

Developing a database

Working in close consultation with the IT department at the DHM, we chose a database from the ACCESS system. Every dataset – whether it involved an object, a room or a cabinet – was assigned a working number that contained both the project's serial number and a respective number to denote inventory, room or cabinet. A data sheet was then set up in the Biocide Database for every working number. Seven different data-entry fields were created on this data sheet for recording object data, different measurements and final assessments.

Investigators entered information for each object measurement in the first data-entry field on the datasheet. It contains a photograph of the object, as well as all object-specific details such as object number, location, provenance, materials/technology, an indicator for whether it had been treated with Eulan and – if known – its restoration history. The Biocide Database is networked with the DHM's inventory database.



Biozid-Messungen

(Projekt 4201 gefördert vom BKM)

Arbeitsnr: BZ_DHM_0004_AK003780_K59-201

ID: 112

Datum: 22.06.2010

Messgerät: TRACER III-SD

Arbeitsnr: BZ_DHM_0004_AK003780_I

GOS-Nummer(n): AK003780

Inventar-Nummer(n): K 59/201

Excel-Datei: S:\Apps\Restaurierung\Biozid

Bearbeiter: Krug,Sonja; Zimmer

Letzte Änderung: 26.10.2010

Nr.: 001
Excel-Sheet: 1
Material: Wolle
Farbe: rot
Anregung: 40kV;5µA; 50 sec;Teflonfilter
Materialstärke: 2,5 mm
Oberfläche: Feintuch, dicht
Datum: 22.06.2010
Ergebnis: 1[illegible]4 ppm Pb
Bewertung:
Bemerkung: Aufbau: Wolle,Seide, Seide Wolle

Nr.: 002
Excel-Sheet: 2
Material: Wolle
Farbe: rot
Anregung: 15 kV; 55 µA; 50 sec; Teflonfil
Materialstärke: 2,5 mm
Oberfläche: Feintuch, dicht
Datum: 22.06.2010

Fig. 4: Data-entry field for XRF-spectroscopy measurement; the result of the marker element testing is circled.

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All details on the object's data-sheet are fed in through this central database.

Three other data-entry fields are earmarked for entries on object measurements resulting from different methods (XRF spectroscopy, UV-Vis spectrometry, organic measurements). They contain details such as date of measurement, type of measuring device, names of staff who performed the measurements, a detailed description of all points measured, as well as the results and an evaluation of the measurements. All of the points measured are mapped on the image of the object. The raw data from every measured point or measurement is listed in an Excel table linked to the data-sheet.

Data-entry fields 6 and 7 are reserved for information on air measurements (taken in the room or cabinet) and dust measurements respectively. In an overview map of all the cabinets housing the collection, the cabinets containing contaminated objects are flagged with a red dot. The air measurement sampling that took place in the depot was oriented around concentrations of cabinets flagged in this way, and was also carried out in the offices of depot staff.

The fifth data-entry field evaluates the results of the results from all of the measurements carried out in each group of measurements (object, air in the room, air in the cabinet, dust). After the project was carried out and evaluated, a PDF file containing all of the details on the project was created for each group of measurements.

A representative range of objects

To ensure a meaningful result, the investigators employed three criteria in their choice of objects for testing from different locations within the textile collection depot. The first was the choice of material. Objects and parts of objects made of wool were the largest group in this category, followed by a group consisting of objects and parts made of fur, hide, feathers and/or leather. The smallest group included objects made of silk, linen and cotton. Most of the articles in question were made of more than one material, such as a uniform jacket made of wool fabric lined with silk, or a military headdress made of wool fabric, leather and silk.

The second criterion used to choose objects was the consideration of an object's status in relation to biocide contamination: was it documented, possible or improbable? Objects that had been tagged as treated with Eulan were included in the study, along with objects that weren't tagged but might have been treated with biocides, and also objects that were believed never to have been treated with biocides.

The third criterion focused on the historic classification and provenance of the objects for study. To choose them, the entire textiles collection at the DHM was first divided on paper into five categories, with importance placed as follows in descending priority and object distribution:

- → Objects formerly in the *Zeughaus* collection
- → Objects repatriated from the Soviet Union after 1945
- → Former MfDG collection (1952–1989)
- → Former DHM collection (1987–1990)
- → Post-1990 purchases.

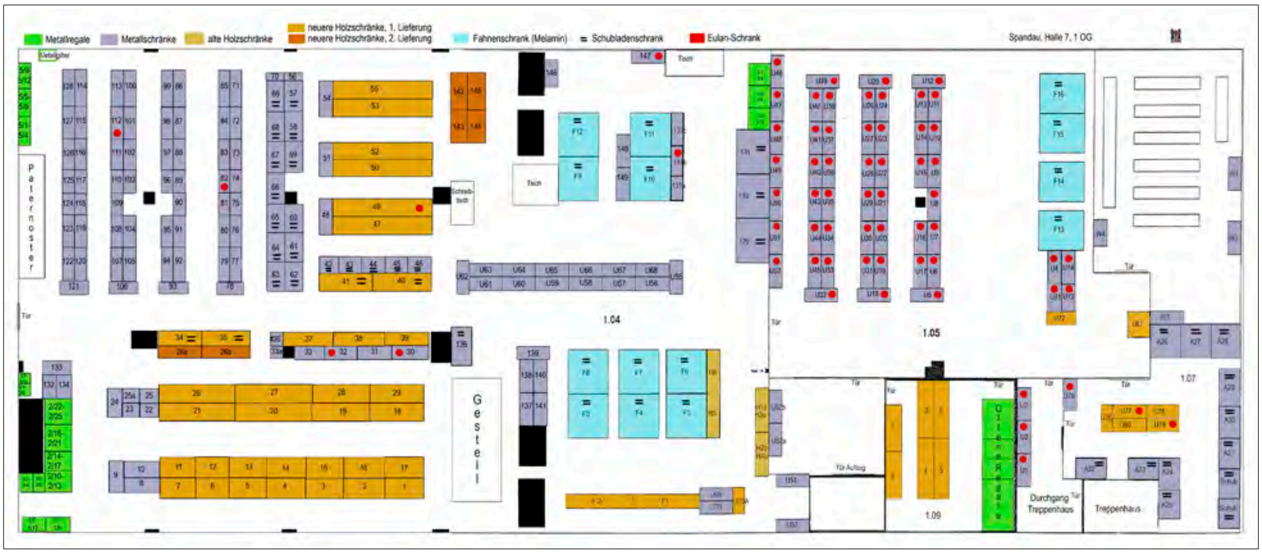

Fig. 5: Plan of the depot; contaminated cabinets are flagged with a red dot.

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Carrying out measurements

To get an idea of the type and extent of the biocide burden in the collection, as well as possible dangers it might pose to staff, the measurement campaigns began with air measurements. Afterwards the XRF spectroscopy and UV-Vis measurements were carried out in tandem. Only after a period of research and preparation of results by experts at the BAM were organic and other additional measurements carried out on the objects.

Air measurements

Emissions testing of room air, air in cabinets and filtered air in climate control ducts was carried out with the TENAX® TA system. Analysis with GC-MS followed.

To ensure that air from the depot rooms didn't disturb ongoing measurements in cabinets, these were taped shut with duct tape after the sensor was mounted in place. Several measurements were carried out in each of the different depot cabinet types: wooden cabinets built before 1970, wooden cabinets built after 1990 and metal cabinets. Wood samples and samples from the material used to seal the cabinets were also taken and tested for the presence of organic biocides.

A further measurement was carried out to test the biocide burden on the air in the DHM's climate control ducts. Intentionally designed to simulate several times the levels that a worker could possibly receive in the course of a working day, the tests were aimed at determining the burden of long-term exposure to contaminated objects. To carry out the study, air filters

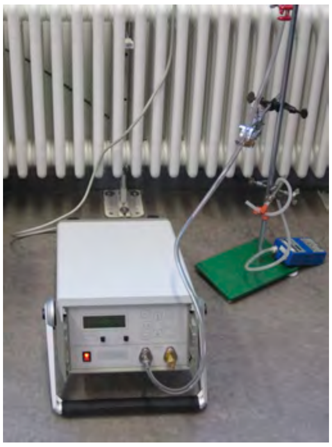

Fig. 6: Measuring air in DHM offices.

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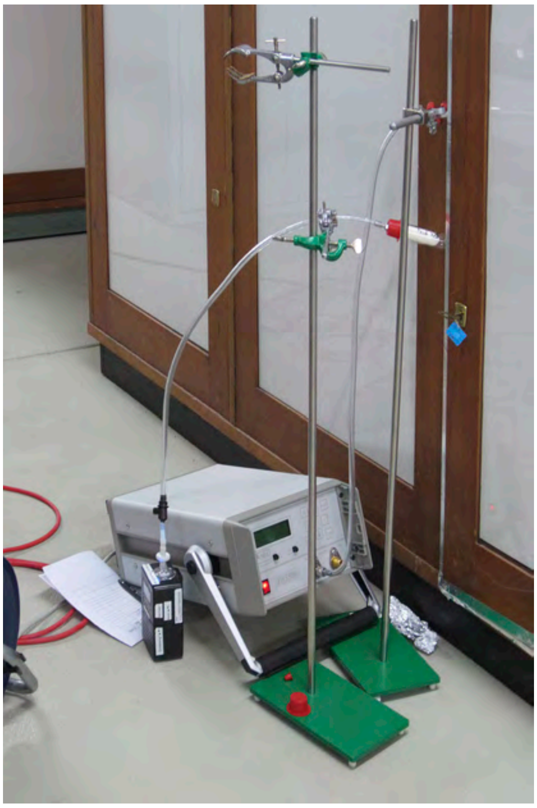

Fig. 7: Measuring the air in cabinets.

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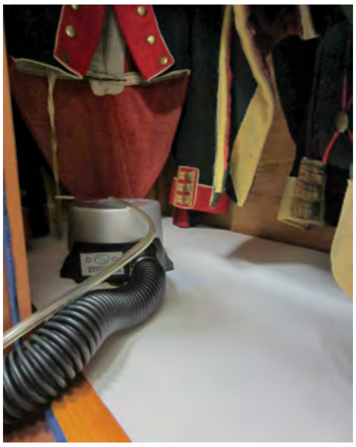

Fig. 8: Air filter measurements, cowling with air filter.

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Fig. 9: Measuring filtered air from cabinets beneath duct cowling.

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were placed in a cabinet with contaminated objects and the air stream was then tested beneath the cowling. As can be seen in Fig. 9, the cowling remained outside the closed cabinet throughout the measurement process.

XRF spectroscopy measurements

The XRF spectroscopy measurements on objects were all taken in the depot within one specifically designated area. Access to the area was blocked by mobile barriers, and warning signs were posted. The measurements were taken by investigators wearing full suits of protective gear, which in this case included a protective tunic, wristbands, chemical-proof gloves and extractors outfitted with Class FFP3 fine particulate dust filters. The German Federal Accident Insurance Fund laid down the guidelines for the protective measures that were implemented. One of the goals of the study was to improve protective measures for staff working under these conditions.

The first set of XRF measurements was carried out with an Artax device, as a mobile Tracer III-SD XRF spectrometer was not yet available. In order to keep contamination within the designated testing area to a minimum, the objects – which had been chosen and entered into the database in advance – were only taken from their cabinets directly before the measurements took place and were removed from the area immediately afterwards. The investigators chose the number and location of points to be measured in advance, but also expanded their scope at times during the procedure.

The measurement protocol was recorded directly in the database while the measurements were going on, and a handwritten duplicate was kept in parallel for later comparison. In the course of the measurement campaign, this method proved to be both robust and very worthwhile, especially when inconsistencies forced a review of both records. Entries into the database were typed in on a laptop that had a protective plastic covering over its keyboard. Typing for investigators was made even more difficult by the protective gloves, and some clerical errors occurred. Verbal communication was also difficult due to the three air-filtering systems. Investigators tested 147 representative objects in total, measuring more than 1,500 points with the XRF spectrometer in all. Each individual point had been analyzed in detail beforehand to determine material, color, structure, layer structure and layer thickness. Each object was photographed, and the points measured were mapped in the investigation protocol.

Based on the spectra revealed by the spectrometer, the BAM later delivered an exact evaluation for each individual point that was tested. Those results were then linked to the appropriate object working number in the database.

UV-Vis measurements

Carried out with an instrument made by GretagMacbeth, the UV-Vis measurements we took at the DHM were both simple and non-destructive. They were performed in parallel with XRF spectroscopy investigations. One reason for carrying out these tests was to determine what dyes had been used in the textiles, but we were also interested in measuring any heavy metals that were present and – if possible – attributing these to specific manufacturing techniques. Even while the study was going on, it became clear that the

Fig. 10: Measuring with an XRF spectrometer.
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Fig. 11: UV-Vis measurement.
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presence of certain elements was not necessarily a sure indicator of biocide contamination, as some of them were used, and indeed still are, in certain manufacturing processes. One typical example is the use of stannous chloride as a component in dyes that employ madder. In cases of this nature, our collaborators at the BAM also analyzed the spectra that resulted from the UV-Vis measurements.

Organic measurements of objects

Contrary to our original plans, we had to take physical samples in order to carry out measurements for organic compounds. The choice of objects for this round of testing was based on amounts of chlorine markers that were detected during XRF testing. As much as possible, samples were removed on or near selected XRF points that had revealed high concentrations of chlorine, using methods that could be justified as minimally invasive. In best-case scenarios, samples of thread could be taken, but in general the samples consisted of fibers taken from the surface of the textile in question.

Threads were only removed from areas that had already sustained damage, from open incisions and seams, or consisted of wool fibers from the surface or hair samples from furs. Taking justifiable, minimally-invasive samples from linen, cotton or silk textiles proved difficult, as fibers from these materials can't be removed from the surface without causing visible damage. Using a thread from the original, a swab sample from what was likely crystallized biocide was removed from one article of livery.

Dust measurements

Swab samples were taken at a number of locations in the depot, as well as from selected, representative objects.

Concluding observations

In retrospect, the investigators are able to say that a key aspect to success in projects of this nature is to prepare for taking measurements as meticulously as possible. At the beginning of our project, planning and prior consultations took up a great deal of the time dedicated to the collaboration. Preparations and measurements were also carried out at the BAM in tandem with the work processes described above – in particular preparations involving measuring devices and desiccator measurements of the objects involved.

The development of the database was a collaborative project. The same goes for the forethought that went into plans for measurements. Before the project began,

Fig. 12: Fiber and thread samples.
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Fig. 13: Crystallized biocide on the surface of a historic textile.
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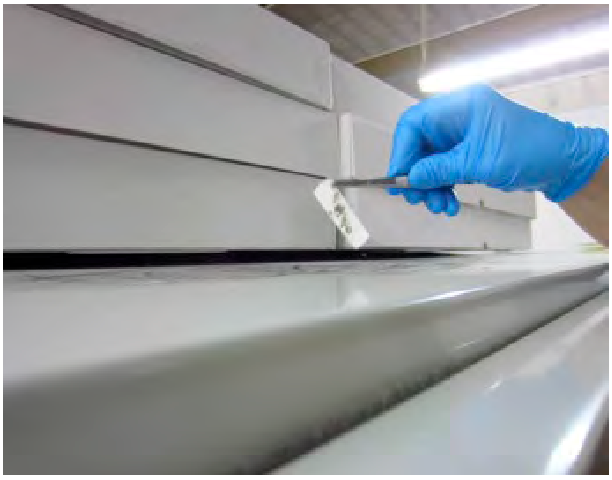

Fig. 14: Collecting a dust sample in the depot.
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everyone involved underestimated the amount of work it would involve. A cooperation that involves natural scientists, restorers and IT experts regularly causes all its members to reevaluate, and often means starting over again in mid-stream. After three years of intense collaboration, however, everyone involved realized not only that we had collected very extensive data in our biocide database, but also that we had all greatly profited from this project.

The work brought us closer to our primary goal, which was to improve our ability to estimate the extent of contamination in the DHM's collections. In addition, the quantification of XRF spectroscopy measurements was improved by improvements to/standardization of existing BAM evaluation methods. The protective gear and clothing for staff that come into regular contact with objects improved dramatically, in particular the combination of gas and dust filters in respirator masks. Out of the difficulties that arose from interpreting measured results, we were able to produce an extensive research project on the use of biocides in a historic context – one that was also able to shed light on the use of heavy metals and chlorine compounds as textile auxiliary agents.

We would like to take this opportunity to thank everyone involved in the project at the BAM for their excellent work and commitment, in particular our colleagues Sonja Krug and Dr. Oliver Hahn, as well as the DHM's Head of Restoration Martina Homolka, the rest of the staff in the museum's Textile Restoration Section, and the computer experts in its IT department.

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1. Two air samples taken by the German Workers Compensation Board (VBG), tests were carried out by the German Institute for Occupational Safety (BGIA). The concentration of the analyzed DDT was 500times lower than the TLV.
2. The study was carried out with an FTIR spectroscope by Dr. Volker Koesling (German Museum of Technology Association Berlin).
3. The study involving two dust samples and one tissue sample was carried out by the BGIA. The presence of DDT, DDE, lindane, Eulan and other methoxychlor compounds was detected, although concentrations were between 0.1% and 0.01% of the total weight tested.
4. UV-Vis spectrometry measures the reflection of radiation in the visible spectrum (wavelengths 380–730 nm).

Oliver Hahn and Sonja Krug

Consequences of historical pest control in archives and museums

Risk assessment – Dangers for humans and the environment

Introduction

Pest infestation by insects is a big problem in many museums and historical buildings. That is why, since the 18th century, toxic agents have been used to attempt to prevent such infestation.[1] The spectrum of effective agents ranges from contact poisons to gases. For example, the use of arsenic in taxidermy has been documented.[2] Mercury's toxic effect on insects has also been known for centuries, as a recipe to combat bedbugs shows.[3] Only in recent times, with the use of inert gases like nitrogen, has a way of killing pests been found that is safe for humans and objects, though it has no preventive effect.[4]

The pesticides used in earlier times, in particular, are toxic substances that, under certain circumstances, emit volatile or low-volatile compounds from the objects and thus can be a danger for humans and the environment. The effective agents employed comprise a broad spectrum of different substances including the aforementioned arsenic and mercury compounds and also lead compounds, but also DDT, PCP, lindane, methoxychlor, triphenylmethane, permethrin, sulfonamide derivates, diphenylurea derivates, phosphonium salts, and other chemicals. In the study, particularly important in the group of organic biocides were DDT, methoxychlor, lindane, and eulan BLN. When and what quantities of which biocides were actually employed is seldom documented; thus, up till now, our level of knowledge has not made it possible to assess the toxicology for employees or possible damage to the works of art.[5, 6]

Analytics

The effective evaluation of biocide burdens was based on the combination of several analytic measuring methods: chemical characterization of organic biocides through emission measurements[7] and vibrational spectroscopy in combination with the characterization and quantification of specific marker elements like chlorine (Cl), mercury (Hg), lead (Pb), and arsenic (As) by means of X-ray fluorescence analysis (XRF.)[8, 9, 10]

The XRF was validated by means of graphite-furnace atomic absorption spectrometry (GF-AAS), cold vapor atomic absorption spectrometry (CV-AFS) measurements for the elements arsenic, lead, and mercury and ion chromatography (IC) measurements for chlorine. A stipulation was that the methods should be nondestructive in relation to the objects.

The focus of the study was on the use of X-ray fluorescence analysis. With the aid of XRF, the elemental composition, especially of inorganic compounds, is identified. The analysis of organic materials is limited with this method. The principle of XRF has been described in detail in diverse publications.[11]

The analysis was done with a handheld spectrometer III-SD from the Bruker Nano GmbH company (Fig. 1). This mobile device is an energy-dispersive X-ray fluorescence spectrometer equipped with a low-power rhodium tube (1 watt), (measuring spot Ø 4 mm) and an energy-dispersive silicon drift chamber detector. Due to the different physical characteristics of the marker elements, the measurements were carried out under two different sets of conditions. The excitation conditions for the element chlorine were: 15 kV, 55 µA, Teflon filter, in a vacuum, with a segment of the energy spectrum up to 15 keV; the excitation conditions for the heavy metals were: 40 kV, 5 µA, Teflon filter, with a segment of the energy spectrum up to 25 keV. The measuring period was 50 s (live time) in all cases.

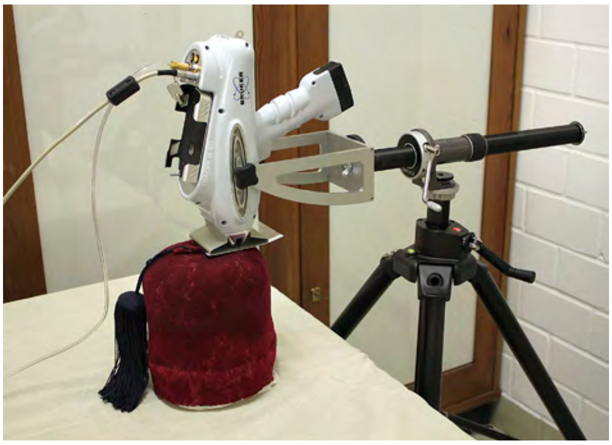

Fig. 1: Examination of a hat by means of X-ray fluorescence analysis.
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Figure 2 shows an ordinary XRF spectrum in which it can be relatively quickly seen which elements are present in the sample. A quantification, however, is more complicated. The signal intensity permits conclusions only about the presence of the various elements and cannot be linearly transposed into the actual amounts of the elements. The latter depends on various parameters, for example the X-ray's depth of penetration, diverse absorption effects, and the detection volume on the respective elements.

The intensities thus differ for the same concentration in accordance with the matrix, surface geometry, and density. For the precise identification of the elemental contents, quantification with external references is needed. To produce the references, various textiles were contaminated with the marker elements. The concentration of elements in the matrices was determined with atomic absorption spectrographic analyses. The net peak intensity determined by XRF shows a linear relation to concentration (Fig. 3). To solve the problem of dependence on layer thickness, several piled layers of a contaminated fabric were measured using XRF. The two illustrations (Fig. 4a und b) depict the dependence of net peak intensity on layer thickness in the examples of lead and chlorine. The net peak intensity of lead initially increases with the thickness of the material: the thicker the sample, the higher the intensity. Only after a certain thickness does the net peak intensity remain constant. The net peak intensity of chlorine is in principle independent of layer thickness (Fig. 5). This can be attributed to the high detection limit for Cl.

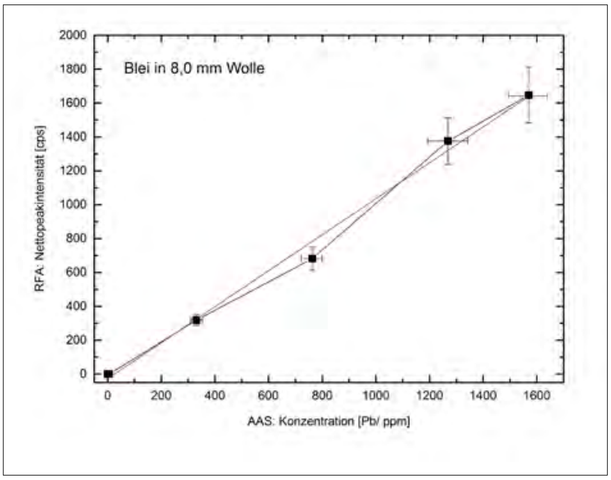

Fig. 3: Net peak intensity as a function of mass concentration.

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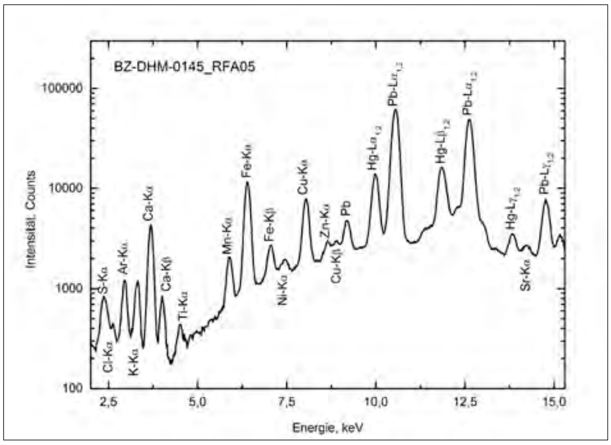

Fig. 2: RX-ray fluorescence spectrum, signal intensity as a function of energy.

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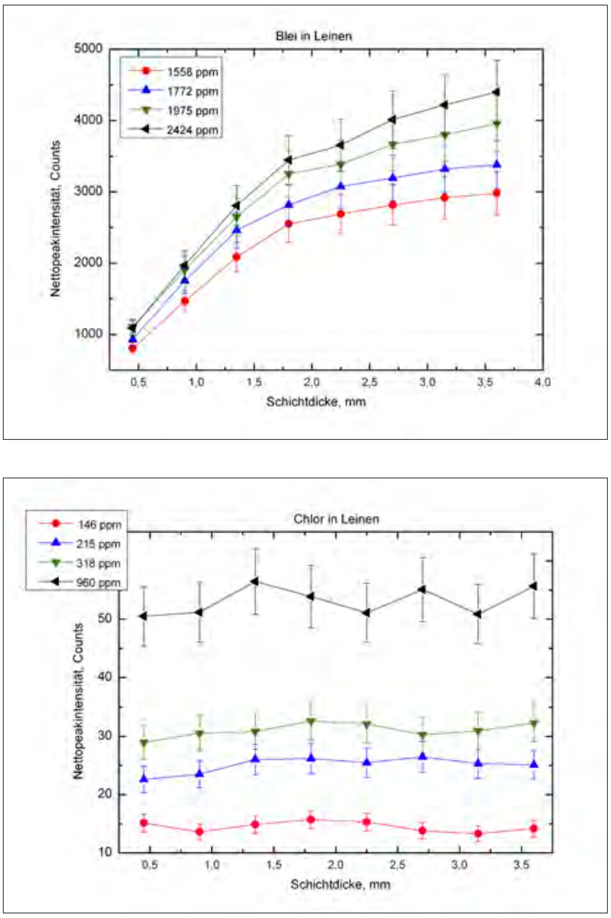

Fig. 4a/b: Net peak intensity as a function of layer thickness. a) lead, b) chlorine.

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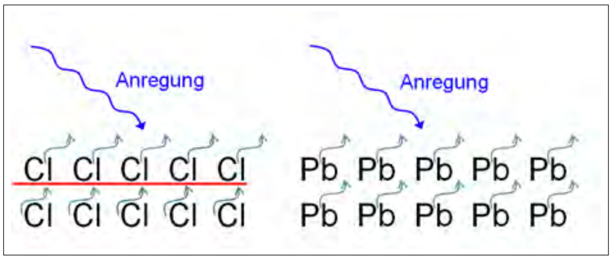

Fig. 5: Model view of energy-dependent absorption of X-rays.

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Results

A total of 147 objects were examined using XRF. The element chlorine was detected in practically all the examined objects. Lead, too, was found in many objects, especially in wool, leather, linen, and silk. In comparison, relatively little arsenic and mercury appear (Fig. 6). This initially correlates with the expectation that many of the objects were treated with organochlorides to protect them from insect infestation. To find out which organochlorides were used, some objects were sampled and the extracted fibers were subjected to direct theromdesorption (see paper by Brödner and Hahn).

Eulan BLN, a low-volatile organic biocide, was detected in all the materials. Lindane, DDT, methoxychlor, paradichlorobenzene, and PCP were also identified.

But can the detected concentrations of chlorine, arsenic, and heavy metals be traced solely to the treatment with biocides? A comparison makes it clear that the presence of chlorine cannot be traced solely to the presence of organochloride biocides. The following table juxtaposes the total amount of chlorine detected in various fibers by means of direct thermodesorption with the content detected by means of XRF.

It is clear that the results do not correlate. The total amount of chlorine detected by XRF is markedly greater than the amount detected by GC-MS. It can be assumed that the difference is due to anionic chloride (salts), which cannot be measured with GC-MS. This chlorine or chloride can stem from the production process (as a stain for textile coloring),[12] storage (dust), or use (sweat and the like). This knowledge can be transposed to the presence of arsenic, lead, and mercury. Mercury was used to produce high-value hat felts,[13] and in the 19th century it was also used in the manufacture of some synthetic pigments. Arsenic compounds were also used in the 19th century to produce aniline pigments[14] and to stabilize blue coloring produced by cold indigo vat dyeing.[15] Finally, salts containing lead are often used as a mordant in textile dyeing.[16, 17]

Tab. 1: Chlorine content, determined by means of GC/MS and XRF

Sample	Cotton	Wool	Fur
GC/MS - Chlorine [ppm]	17	27	6,609
XRF - Chlorine [ppm]	1,100	3,179	66,104

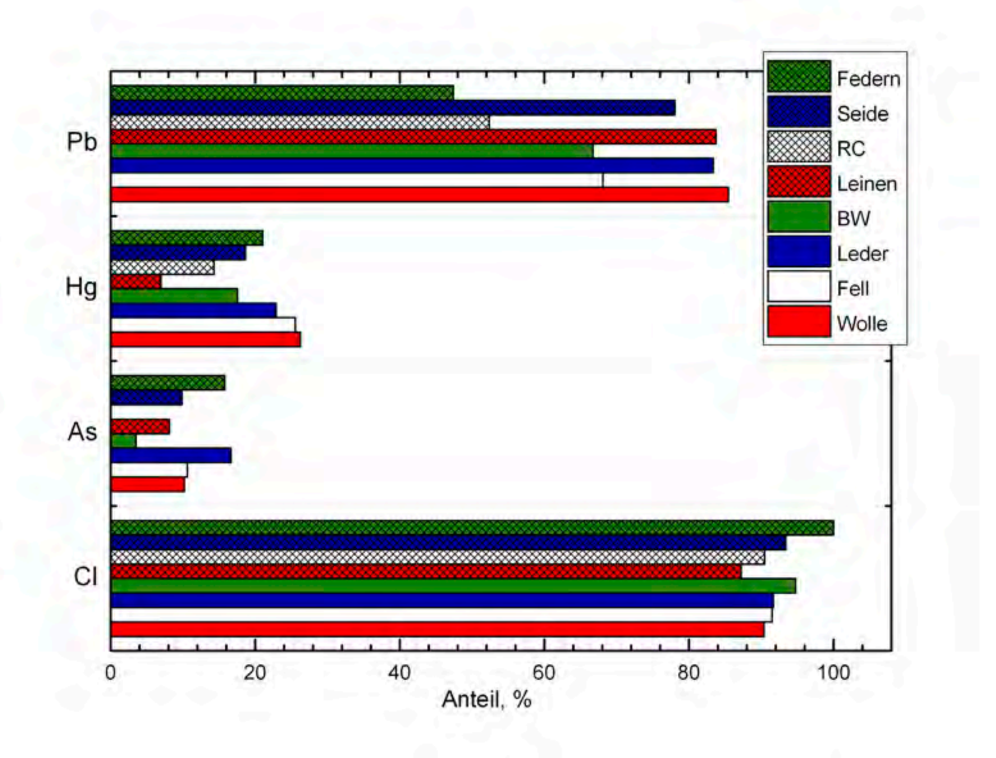

Fig. 6: Qualitative results of XRF in overview.

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Conclusion and Prospects

With X-ray fluorescence analysis, a low-priced, practical method was employed for the nondestructive detection of the elements chlorine, arsenic, and diverse heavy metals in textile samples. A quantification routine was developed that, supported by suitable reference materials, makes it possible to precisely determine the amounts of elements in the textiles.

Vibration spectroscopic examinations did not lead to the desired result, the nondestructive identification of the chemical composition of the biocides.[18] For this reason, we resorted to a minimal-invasive sampling to extract and analyze the organochloride biocides contained in the samples by means of direct thermodesorption. We were able to show unambiguously which volatile compounds were emitted into the room air and which were not.

It can thus be considered to be secured that toxic compounds are contained in the textile objects, so that protective clothing is definitely advised when dealing with these objects. Such protective clothing includes gloves, a smock, and adequate respiratory protection. Due to the pollution of the air in the depot cabinets, a dust mask alone is not sufficient. A dust mask prevents contamination by dust-bonded biocides, but does not protect against lindane or naphthalene. Regular thorough dust cleansing is also recommended as an additional measure.

Many chemicals that are categorized today as allergenic or toxic compounds did not enter the objects through the use of biocides. These are often compounds clearly used in the manufacturing process. A removal or extraction of these compounds is thus not striven for per se, since this would be a major intervention in the character of the objects.

Acknowledgements

The project “Consequences of historical pest control in archives and museums. Risk assessment – danger for humans and the environment” was funded by the Commissioner for Culture and the Media (BKM) under the registration number AZ K 41 – 300 015. We would like to thank Martina Homolka, Andrea Lang, and Judith Zimmer from the DHM for the successful collaboration, along with Doris Brödner (BAM, Department 4.2) for carrying out and evaluating the emission and thermodesorption measurements, Holger Scharf and Heike Witthuhn (BAM, Department 1.1) for carrying out the GF-AAS and CV-AFS measurements, Oliver Krüger (BAM 4.4) for carrying out the IC measurements, and Ulrich Waldschläger (Bruker AXS) for carrying out the TXRF measurements. We also thank Ira Rabin (BAM, Department 4.5) and Roald Tagle (Bruker Nano), in particular, for their constructive criticism.

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Doris Brödner and Oliver Hahn

Identifying volatile organic compounds using gas chromatography coupled with mass spectroscopy

At the German Historical Museum (DHM), a risk for humans and the environment was assumed, because treatment with biocidal agents had been documented and was known.[1] Many objects in the textile collection are marked with a eulan tag, the certification that the objects had been eulanized, i.e., treated with a group of chloranalids that were subsumed under the name "EULAN".[2] Beyond that, in past measuring campaigns, other organochlorides were detected in the room air of the depots and in the dust.[3]

Gas chromatography and subsequent mass spectroscopy were to be used to detect these volatile organic compounds in the depots and exhibition showcases.[4, 5]

Examining the room air by measuring emissions

The basics for conducting emission measurements and for designing the emission testing chambers have been described in several European reports.[6] Norm DIN V ENV 13419, parts 1-3, worked out in CEN TC 264, WG 7, addresses the characterisation of emissions of volatile organic compounds using emission testing chambers or emission measurement cells and obtaining, treating, and preparing the emission samples.[7]

To take the samples of the volatile organic compounds (VOC) from the room air, the emitters to be analyzed were collected via a constant stream of air through absorption on Tenax® TA (polyphenyleneoxide, Fig. 1).[8] The sampled Tenax tubes were thermodesorbed, and the VOCs were transferred through a cold trap to the gas chromatograph.[9, 10] The subsequent gas chromatographic separation was carried out with a DB5 – MS capillary column (0.25 µm layer thickness; 0.25 mm interior diameter and 60 m length). The gas chromatograph is equipped with a mass spectrometer as detector. With the methods used, the limits of detection for the various VOCs lie below 1-2 µg m^{-3}. This paper will not discuss special sampling procedures to detect acetic acid or formic acid[11] or to analyze aldehydes and ketones.

The emission measurements (Fig. 2) revealed naphthalene, paradichlorobenzene, and lindane. The determined concentrations of biocides in the room air lie below the permitted levels (Tab. 1). In the cabinets, the concentrations are substantially higher than in the room air, i.e., the ventilation systems filter the toxins almost completely from the room air.

Fig. 1: Tenax® TA tube.

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Fig. 2: Room air measurement in the depot of the DHM.

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Tab. 1: Results of the emission measurements (all data in µg biocide per m^3 room air)

	Room air (depot) (Σ 5 measurements)	Depot cabinets (Σ 11 measurements)	Permitted level
	[µg/m^3]	[µg/m^3]	[µg/m^3]
Naphthalene	0 – 9	8 – 425	500[12 + 13]
p-Paradichlorobenzene	*0 - <cal*	4 – 84	6000[32 + 33]
Lindane	0	4 – 9	100[14]

Direct thermal desorption

Although it is documented that the objects were treated with eulan, it was not possible to detect the presence of chloranalides. So, in the further course of the study, we decided to take small samples, i.e., individual fibers, from the objects and subject them to a direct thermodesorption. To do this, the fiber samples were baked out of a glass tube (Fig. 3) and then analyzed using GC/MS.

The analysis is carried out in the same way as with the Tenax tubes, described above. The glass tubes filled with fiber samples are thermodesorbiert in a GERSTEL thermodesorber with a downstream cold trap. (Fig. 4). With this method, it was possible to detect organochlorides directly from the textiles, for example EULAN BLN (Fig. 5, Fig. 6a-c; on this, compare also Lichtenstein et al., note 2). This was not possible with conventional room air measurements or by means of a sample taken by solid phase micro-extraction (SPME).[15]

In all the materials examined, EULAN BLN was detected as a low-volatile organic biocide.[16] Lindane, DDT, methoxychlor, paradichlorobenzene, and PCP were also detected. An additional biocide, naphthalene, was analyzed in all samples.

Fig. 3: Glass tube with fiber samples for thermal extraction.
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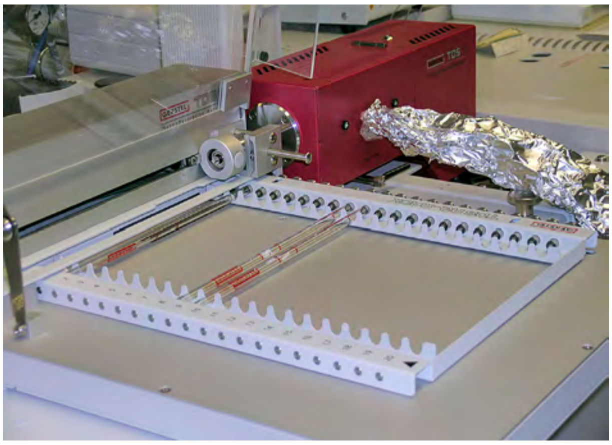

Fig. 4: Glass tube in auto-sampler.
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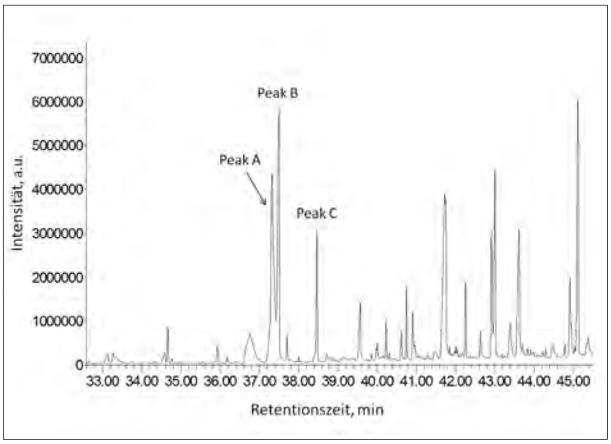

Fig. 5: Gas chromatogram of a thermally desorbed textile fiber. The peaks labeled A, B, and C indicate EULAN BLN.
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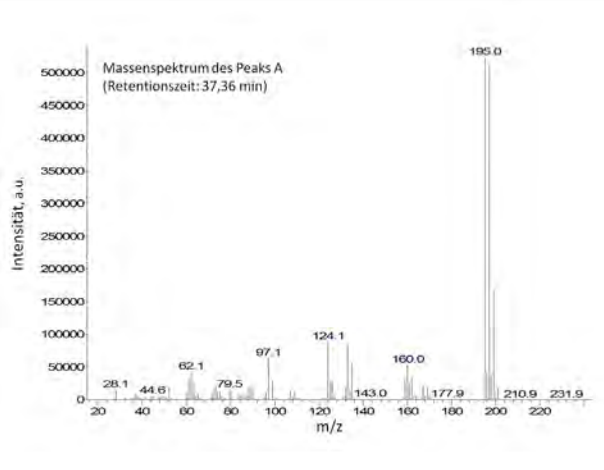

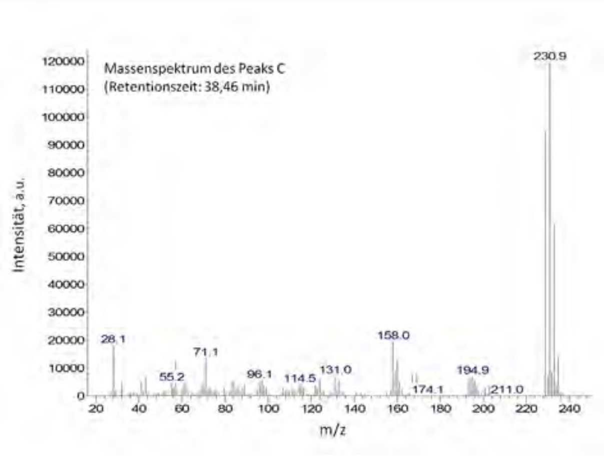

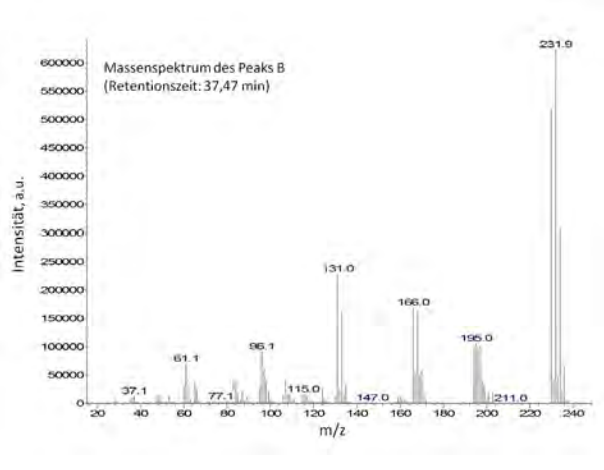

Fig. 6a – c: mass spectra of the peaks A, B, and C that contain characteristic fragments of eulan BLN.

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Tab. 2: Results of the direct thermodesorption (all data in ng biocide pro mg sample)

	Fur	Cotton	Silk	Silk	Silk	Wool	Wool	Wool	Wool
	[ng/mg]	[ng/mg]	[ng/mg]	[ng/mg]	[ng/mg]	[ng/mg]	[ng/mg]	[ng/mg]	[ng/mg]
Eulan-BLN	56	336	56	51	84	511	158	181	336
***p*-Paradichloro-benzene**	–	–	–	–	–	–	–	–	0.2
Naphthalene	8	3	10	2	0,4	15	30	2	2
PCP	nq[17]	0.3	–	–	–	4	–	nq	0,5
Lindane	1	0.3	nq	2	–	6	1	4	1
p,p‘-DDT	4	–	–	–	–	–	–	57	6
Methoxychlor	3	–	–	–	–	–	–	21	19

Conclusion

Not all the organochlorides with which the textiles were treated (see Tab. 2) gas off in the room air or cabinet air. It was not possible to identify either EULAN BLN or methoxychlor by measuring emissions. Apparently, physico-chemical interactions "anchor" the compounds so tightly to the textile fibers that they do not emit under normal conditions. Further measurements also detected these compounds in various dusts (compare the aforementioned measurements conducted by the *Institut für Arbeitsschutz* of the *Deutsche Gesetzliche Unfallversicherung*).

In the framework of the research project, it was unambiguously shown which volatile compounds were emitted into the room air and which were not. Among the organochloride biocides that emit into the room air are paradichlorobenzene and lindane; naphthalene was also detected. Additional organochloride compounds, like EULAN BLN and methoxychlor, could not be detected in the room air, but were detected directly on the textile fibers or in the dust. Other substances containing either arsenic or heavy metals (Hg, Pb) were detected either in the textiles themselves or in the dust (on this, compare the paper by Krug and Hahn).

It can thus be considered to be secured that toxic compounds are contained in the textile objects, so that protective clothing is definitely advised when dealing with these objects. Such protective clothing includes gloves, a smock, and adequate respiratory protection. Due to the pollution of the air in the depot cabinets, a dust mask alone is not sufficient. A dust mask prevents contamination by dust-bonded biocides, but does not protect against lindane or naphthalene.

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Andrea Lang and Judith Zimmer

Manufacturing-Related Ingredient or Applied Biocide?

An attempt to interpret the measurement results in the context of the application

Even in collections that are not known to have been treated with pesticides, objects may be contaminated with substances containing biocidal substances, such as arsenic, lead, and chlorine and/or mercury compound. Conservators and other museum staff who come into direct contact with the objects must be protected from possible harmful effects. The presence of such contaminants does not necessarily indicate the use of biocides applied to combat pests, but may be related to the manufacturing processes itself. A number of concrete examples will show that the detection of elements such as chlorine, mercury, arsenic or lead using X-ray fluorescence analysis (XRF) requires cautious evaluation and does not necessarily indicate pesticide treatment. Only further identification of the particular organic or inorganic compounds can provide clarity about the source of the contaminants and about the history of their application.

In the course of the three-year research project there has been considerable discussion about protecting objects from damage through applied biocides, about potential destruction to the original material during the investigations – and about the pros and cons of decontaminating objects containing toxic substances. These considerations were not only related to the measuring techniques and the distinction between non-destructive measurement and minimally invasive procedures, but also to the issue of the extent to which decontamination might remove elements or compounds related to the manufacturing process or to the object's history.

In this connection we would like to ask the question of whether during a decontamination it would be possible to distinguish between an applied biocide and an ingredient related to the manufacture. To provide data for this debate we have carried out initial literature searches on manufacturing techniques for textiles and leather in the corresponding historical periods. Here we present the result of this study based on several selected objects, without any claim to completeness. In parallel, all references to the use of biocides in the collections of the German Historical Museum (DHM) were compiled from the museum archive. In the course of the measurements more than 1,500 data points were obtained for more than 147 representative objects.[1]

Analysis of the measurement results confirmed the suspected presence of certain marker elements as indications of biocide treatment of the objects. The four marker elements mercury, arsenic, lead and chlorine were selected from the group of detected elements and the levels of these four elements are presented in the following table.

It is apparent from the second column that the elements chlorine and lead are often present in the DHM textile collections. The frequency of mercury and arsenic is slight by comparison – although individual cases are interesting and worthy of discussion. There is a considerable variation in the concentrations (in ppm) between the measurement points. All four elements exhibit so-called outlier values in both directions – that is, they are detected at both vanishingly

Tab. 1: Analysis of the XRF-measurements

Element	Number of objects	Fraction of 147 objects in %	Measured concentration range in ppm[2]	Typical concentrations in ppm
Mercury	10	6,8	13–7,576	large variation
Arsenic	9	6,1	6–370	50–75
Lead	107	72,8	0,36–23,181	130–550
Chlorine	139	94,6	152 –182,652	1,000–5,000

Tab. 2: References of biocide treatments at the Museum of German History, MfDG (1952–1989)

Hydrogen phosphide, also phosphine	Documented in Neue Museumskunde 1972[3]
Eulan, EULAN®BLN	Documented in contemporary file memos[4] and stamped labels in the objects
Woguman C	Documented in contemporary file memos[5]
Haka Mottentod	Documented by a package found in an object
Camphor	Verbal account
Naphthalene	Verbal account
Mothproofing paper	Verbal account

small traces and extremely high concentrations. A look at the individual measurements shows that the chlorine concentration for most of the measurements ranged between 1,000 and 5,000 ppm. Typical concentration values for the element lead lie in the range of 130 to 150 ppm.

The analysis of the mercury results requires a more individual approach. This element occurs in only trace amounts and the values fluctuate so strongly that it is not possible to make out a 'typical' concentration value. This suggests that the presence of mercury is related to manufacturing processes; indeed in the case of certain objects this is almost certainly the case.

Arsenic is also present in relatively minor quantities. The average measured value lies around 65 ppm, with 'outliers' extending down to 6 ppm and up to 370 ppm.

The literature search uncovered a number of examples of applications and recipes involving one or several of the four measured marker elements. The most frequent use of lead, chlorine and mercury is found in mordant, dyes and dyeing formulas. We searched the literature from around 1780 to the present day in order to determine which manufacturing process best fit the date of the object. This research is still ongoing.

The correlation of the literature recipes was aided not only by the results of the inorganic and organic XRF measurements, but also by the results of VIS spectrometry, which enabled the dyes used in the manufacture to be identified.

Confirmed Data on Biocides used in the DHM Collections

The research in the museum archives and questions put to longstanding museum staff provided documentation and verbal accounts of a number of biocide treatments carried out on the collections (Tab. 2).

We have been able to find documentary evidence of the use of at least four different biocides as well as verbal accounts of the use of naphthalene and camphor. There is also certainty regarding the use of assorted undocumented mothproofing papers and similar products.

Use of the Four Marker Elements as Pesticides and in Production Processes

In the following sections examples of usage of the individual marker elements as well as their possible applications as biocides are investigated based on literature references.

The Use of Mercury as a Biocide

Our research to date shows that mercury has rarely been recommended for use as a biocide, since its hazards to human health were long recognized. However a recipe from 1825 describes the production of a household agent to combat bedbugs:

"Take 2 lots of mercury and the white of 5 eggs, beat the two in a bowl with a brush or whisk until no mercury globules can be seen, then take apart the beds, thoroughly rub all joins and cracks with this liquid and allow to dry. On first use most of the bedbugs will die, and after further application of this agent not one will remain."[6]

Preservation of scientific collections using mercuric chloride is frequently mentioned in the literature, but is not recommended by Rathgen 1924 who notes that this type of treatment is not sufficiently long-lasting.[7] Still we cannot rule out the possibility that biocide

Tab. 3: The Use of Mercury as a Biocide

Compound Name, Synonyms, Trade Name	Chemical Formula	Use	Source
Mercury	Hg	Insecticide against bedbugs	N. N. 1829
Mercury(II) chloride, *also* mercuric chloride, mercury bichloride, *or* corrosive sublimate	$HgCl_2$	Biocide in natural history collections	Rathgen 1924

treatments using mercury did occur, since Rathgen's views would not have been known to all collectors at all times.

The Use of Mercury in Manufacturing Processes

The use of mercury in production is far more widespread and diverse than its application as a pesticide. Its use in treating hare or rabbit fur to make felt for hats is well known. As late as 1912 the feltware trade journal "Filzwaren-Markt" was still writing about the poisoning of hatmakers by mercury:

"This was discussed in detail by Professor Tylecote in his lecture at the International Congress of Hygiene. The hair mostly from rabbit fur used in making hat felt is still being treated with a substance that can and must cause an occupational disease, namely a solution of acid nitrate of mercury. Among furriers this process is called carrotting because carrot oil was once used for this purpose, although it was abandoned as unsuitable some time ago. Since then the danger of mercury poisoning for hatmakers has been adequately demonstrated, yet so far there has been no fundamental change in the form of an elimination of this toxin. (...) Dresden 20 December 1912."[8]

Mercury was also used in the manufacture of aniline dyes and as a mordant for coloring silk.[9]

The Use of Arsenic as a Biocide

In studying the relevant literature of the respective periods it is notable that it only issues warnings about arsenic. In contrast to lead, chlorine and, in part, mercury, arsenic had long been known and feared as a potent and dangerous poison.[11]

Rathgen 1924 expressly recommended the conservation of furs, hair and feathers in natural history collections by dipping or spraying the objects with an alcoholic solution of sodium arsenate as a protection against moths.[12]

One hundred years earlier arsenic had been recommended and used as an effective poison to combat larger pests in the household:

"Arsenic is finally also being used very frequently to kill and eradicate pests like rats, mice, cockroaches, flies, etc, whereby it is hardly necessary to point out that this application must always be carried out with the greatest caution; in any case white arsenic should never – as per regulation in Bavaria – be used for this purpose in pure form, but only in its colored state in combination with indigo, soot, Prussian blue etc. in order to avoid poisoning in humans as far as possible."[13]

Tab. 4: The Use of Mercury as a Manufacturing Processes

Compound Name, Synonym, Trade Name	Chemical Formula	Use	Source
Mercury(I) nitrate, *also* mercurous nitrate	$Hg_2(NO_3)_2$	Pickling fur for the production of high-quality hat felt; Synthesis of the red aniline pigment known as "Azaleine" (magenta)	Leuchs 1831 Filzwarenmarkt 1924 Glafey 1937[10] Leuchs 1863
Mercury(I) oxide, *also* mercurous oxide	Hg_2O	High-gloss black coloring for silk	Leuchs 1839
Mercury (II) sulfate, *also* mercuric sulfate	$HgSO_4$	Synthesis of the aniline pigment Prussian blue ("Parisian blue")	Leuchs 1863

Tab. 5: The Use of Arsenic as a Biocide

Compound Name, Synonym, Trade Name	Chemical Formula	Use	Source
Arsenic(III) oxide, *also* arseneous oxide, arsenic, white arsenic	As_2O_3	Household rodenticide and biocide for cockroaches; often colored with indigo	Reinsch 1843
Sodium arsenate, *auch* sodium dihydrogen arsenate	H_2NaAsO_4	Preservation of hides in collections	Rathgen 1924[14] Lehmann[15]

Tab. 6: The Use of Arsenic as a Manufacturing Processes

Compound Name, Synonym, Trade Name	Chemical Formula	Use	Source
Arsenic acid, *also* arsoric acid	H_3AsO_4	Reagent in the synthesis of aniline dyes	Leuchs 1863 Buchheister 1893[17]
Arsenic(III) sulfide, *also* arsenic trisulfide , arsenic yellow, opiment, sulfuret of arsenic, king's yellow	$As_2 S_3$ or As_4S_6	Yellow dyeing: "first treat the fabric with lead suger and then add it to a solution of arsenic sulfide (...) in potash";[18] Stabilizer for blue dyeing with cold vat indigo	Leuchs 1831 Krünitz 1773–1858

The Use of Arsenic in Manufacturing Processes

The arsenic applications described here are merely a small fraction of the recipes discovered in the course of our research. Arsenic was used both in the production of dyes and in the dyeing process itself.

According to Krünitz 1773–1858, the addition of arsenic-containing orpiment stabilized the blue coloration of the indigo vat in silk dyeing:

"The cold indigo vats are often claimed not to be useful enough and that they do not produce a good dark blue, but that is an error; the mistake is simply that the practitioner has used too little orpiment, or, instead, arsenic on its own. As long as one follows the instructions given here, carefully grating the indigo ahead of time and washing it in water, then it can be used with great usefulness and comfort and yield just as much dark violet and an even more beautiful blue as from the warm vat."[16]

The Use of Lead as a Biocide

The biocidal action of lead has also been known for a long time. For example, it was widely used in combination with arsenic in the form of lead arsenate as an insecticide in farming. Lead acetate, also known as lead sugar, is mentioned in the literature[19] as a poison for mice and other large pests. In an 1872 issue of E. M. Dingler's "Polytechnisches Journal" the use of lead acetate is recommended for mothproofing during fabric finishing[20]. So far, the only indications we have that it was also used in museum collections and on objects to control pest infestation come from verbal accounts.

In the course of this project we have detected lead relatively frequently in the selected objects – in 107 of 147 cases. This suggests that at least some of these objects were contaminated with lead acetate due to its pesticidal action. However, repeated questioning of colleagues regarding the use of lead sugar as a biocide in museum collections has so far produced no concrete evidence.

Tab. 7: The Use of Lead as a Biocide

Compound Name, Synonym, Trade Name	Chemical Formula	Use	Source
Lead(II) acetate, *also* lead diacetate, lead sugar, plumbous acetate	$Pb(CH_3COO)_2$	Toxic feed bait for control of mice and other large animals	N. N. 1829
Lead acetate	$Pb(CH_3COO)_2$	Mothproofing	N. N. 1872
Lead acetate	$Pb(CH_3COO)_2$	Pesticide in museums and collections	Verbal account
Lead hydrogen arsenate, *also* lead arsenate	$PbHAsO_4$	Insecticide	GESTIS Substance Database[21]

Tab. 8: The Use of Lead as a Manufacturing Processes

Compound Name, Synonym, Trade Name	Chemical Formula	Use	Source
Lead acetate	$Pb(CH_3COO)_2$	Mordant for dyeing	Krünitz 1773–1858
Lead acetate	$Pb(CH_3COO)_2$	Mordant for cotton printing	Pierer 1841[29]
Lead acetate	$Pb(CH_3COO)_2$	Making leather elastic and water-repellent	Krünitz 1773–1858
Lead(II) carbonate, *also* basic lead carbonate white lead	$2\ PbCO_3Pb(OH)_2$	White pigment, whitening of glacé leather after tanning	Krünitz 1773–1858
Lead(II) chromate, *also* *Chrome Yellow*	$PbCrO_4$	Mordant dye	Krünitz 1773–1858
Lead(II) oxide, *also* plumbous oxide, massicot	PbO	Dyeing animal skins	Pierer 1841[30]
Lead (IV) oxide, lead dioxide, plumbic oxide	PbO_2	Brown to black dyeing of wool	Leuchs 1831
Lead(II) hydroxide, *also* lead hydroxide, plumbous hydroxide	$Pb(OH)_2$	Mordant for cochineal dyeing	Arppe 1845[31]
Lead(II) sulfate, *also* lead sulfate	$PbSO_4$	Resist paste[32] for vat dyeing	Glafey 1937[33]

The Use of Lead in Manufacturing Processes

We were able to find numerous references to the use of lead in the finishing of textiles or clothing.[22] For example, lead sugar was used in the dyeing of silk, especially for red tones.[23] Lead(II) chromate, better known as Chrome Yellow, was indispensible in the 19th and 20th centuries for the production of highly brilliant yellow[24] and red[25] tones. Other lead compounds were used to dye wool brown to black hues[26], and to whiten[27] glacé leather. In Krünitz 1773-1858 we find the description of a patent from the year 1794 for a process for making leather water-repellent and elastic.[28] This formula was presumably widely used in the production of soldiers' boots.

The Use of Chlorine as a Biocide

The following table contains a selection of the major organochlorine compounds that were used in the 20th century as biocides and, in part, are still used today. The list includes DDT, the pesticide compositions called Eulan, Globol (a brand of p-DCB), lindane, Woguman C (an East German brand), and pyrethroids such as permethrin. The use of most of these substances in the collections of the DHM has been confirmed. At this

Tab. 9: The Use of Chlorine as a Biocide

Compound Name, Synonym, Trade Name	Chemical Formula	Use	Source
Dichlorodiphenyltrichloroethane (DDT)	$Cl_4H_9Cl_5$	Insecticide	Lehmann 1965[34] Odegaard, Sadongei et al. 2005[35]
Eulan	several	Mothproofing agent	Unger 2012[36]
1,4-Dichlorobenzene (Globol)	$C_6H_4Cl_2$	Mothproofing agent	Rathgen 1924[37]
γ-Hexachlorocyclohexane (Lindane)	$C_6H_6Cl_6$	Insecticide	Lehmann 1965[38]
Methoxychlor (Woguman C)	$C_{16}H_{15}Cl_3O_2$	Insecticide	Homolka 2013[39]
Permethrin (pyrethroid)	$C_{21}H_{20}Cl_2O_3$	Insecticide	Odegaard, Sadongei et al. 2005[40]
Mercury(II) chloride, *also* corrosive sublimate	$HgCl_2$	Insecticide	Rathgen 1924[41]

Tab. 10: The Use of Chlorine as a Manufacturing Processes

Compound Name, Synonym, Trade Name	Chemical Formula	Use	Source
Chloroacetic acid	$C_2H_3ClO_2$	Indigo synthesis	Merck's Warenlexikon 1924
Chlorine, *also* chlorine gas	Cl_2	Bleaching	Leuchs 1845
Chlorine powder	Technical mixture	Bleaching	Leuchs 1845
Potassium chloride	KCl	Bleaching	Leuchs 1845
Sodium chloride, *also* common salt solution	NaCl	SSoupling silk	Leuchs 1845
Hydrochloric acid	HCl	Bleaching	Leuchs 1845
Tin(II) chloride, *also* stannous chloride, tin salt, vat tin	$SnCl_2$	Dye mordant for various red colors, reducing agent in indigo dyeing	Krünitz 1773–1858 Krünitz 1773–1858
Tin(IV) chloride, *also* stannic chloride, pink salt	$SnCl_4$	Since 1630 in cochineal dyeing	Meyers großes Konversationslexikon 1905

point we should also mention the inorganic biocide mercury(II) chloride, which also contains the marker element chlorine.

The Use of Chlorine in Manufacturing Processes

Although the element chlorine was not discovered until 1774, chlorine-containing compounds had been used much earlier for making and finishing textiles; they have been documented in the literature for more than 400 years. To name a few prominent examples: as early as 1630 Dutch dyers used stannous chloride as a mordant for cochineal dyeing.[42] In the following centuries tin chlorides were used as mordants for a number of red tones,[43] as reducing agents for indigo[44] and in cotton printing.[45] Various aqueous solutions of chlorine compounds as well as chlorine vapors or gases found massive use as bleaching agents in the late 18th century.[46] Solutions of common salt were used for the 'soupling'[47] – that is, the opening up and degumming of raw silk – and chloroacetic acid became immensely important in the production of synthetic indigo.[48]

Attempts at Interpretation

In the following sections we show using the examples of selected objects how the concrete measurement results can be interpreted and placed in the context of the application.

Livery of a Page at the Prussian Royal Court

Fig. 1 and 2: Locations of points for XRF and VIS measurements on the front and back.

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The first interpretation of the results of marker element measurements will be shown using the example of a page's livery from the Prussian royal court, dated around 1899. This object was selected for the interpretation because it exhibited a broad range of marker elements (Tabelle 11).

The value for chlorine at the measurement points varied between 1,114 and 21,864 ppm. Lead was unambiguously identified with a slightly fluctuating value of 118 to 230 ppm. Measurements of the lining of the livery showed arsenic to be present at a value of 75 ppm.

The results for lead are consistent with both possibilities. On the one hand, compounds of lead are known from the literature to have been used to make dyes and in the dyeing formulations. On the other hand, the homogeneous distribution of the lead on the three different fabrics – red woolen cloth, black silk velvet and blue silk lining – could also be interpreted as the result of treatment with a lead-containing substance as a biocide.

Tab. 11: Concentration range in ppm

Chlorine	1,113–21,864
Mercury	168 (in the black velvet cuffs of the sleeves)
Arsenic	75 (blue silk lining)
Lead	118–230
Chromium	trace amount, not quantified (in the black velvet cuffs of the sleeves))
Copper	trace amount, not quantified
Zinc	trace amount, not quantified

Tab. 12: Lead concentration in ppm

01/02: 124
03/04: 118
05/06: –
07/08: 230 (silk lining)
09/10: 153
11/12: –

The point labeled 05/06 in Figure 2 refers to a measurement of the lining in which arsenic was found. The silk fabric of the lining has a dark-blue color that was identified with the help of a VIS spectroscopic measurement at point 07/08 as indigo dye, shown as the blue curve in Figure 3.

The result of the VIS measurement showing indigo dye suggests that the arsenic found in the blue silk lining is due to an addition of orpiment to the indigo cold vat. A subsequent biocide treatment of the object with an arsenic-containing formulation seems unlikely, and can be ruled out for the time being since there was no indication of arsenic in the red wool. Arsenic was only detected in the lining of the livery. Analysis of the VIS curve for the red woolen cloth showed it had been dyed with madder. This result – combined with the admittedly small amount of tin – suggests the use of a tin mordant during the madder dyeing of the wool.

This example shows how important it is to correctly map the measurement points and to take care in analyzing and describing them. Only then can the measured elements be clearly correlated with the manufacture and/or biocide application.

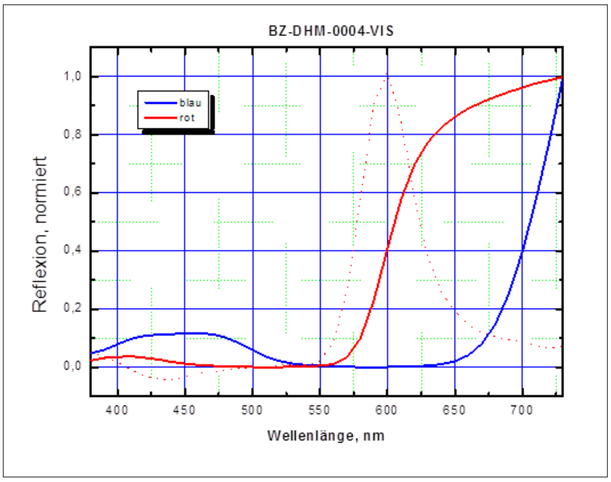

Fig. 3: VIS measurement of the livery.

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Bicorne for a General, worn by King Frederick William III

Fig. 4: Locations of points for XRF measurements.
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The second example we would like to present here is a bicorne dating from the early 19th century.

Alongside very high values for chlorine and lead, the bicorne exhibits a very high mercury concentration.

The hat felt is made of hare or rabbit fur. To prepare the hairs for feltmaking, they were treated with a solution of mercuric nitrate.[49] The literature shows that hats were dyed black with mercury. The exceptionally high mercury value in the silk bow may be due to the silk being dyed with mercurous oxide, which produced an especially glossy color.[50]

However it is also possible that the object was treated with mercury chloride as a biocide. This possibility should not be ruled out in further investigations, as the bicorne is part of the historical Zeughaus collection, the oldest part of the DHM's collection.

Tab. 13: Concentration range in ppm

Chlorine	1,028–9,508
Mercury	4,699–7,160
Lead	151–215
Iron	not quantified
Copper	not quantified
Zinc	trace, not quantified

Alongside the documented treatment with organochlorine pesticides after 1945 we would like to draw attention to a possible manufacture-related use of chlorine. There is a recommendation from the period for treating felted hats in a 'chlorine bath' to facilitate the subsequent black dyeing. The recommendation refers to wool felts, but this does not necessarily exclude fur-based felts:

"According to Raymond, chlorine makes the wool – when it is treated in a solution of the same – soft and supple, probably by destroying the rough parts of the wool. However it then loses its ability to be felted and walked, but takes up iron oxide much more easily, enabling it to be dyed a stronger black. Thus hats after felting and cloth after walking can be softened and more readily dyed black through treatment with chlorine."[51]

The recommended degumming of silk using a solution of common salt could also be responsible for enhanced levels of chlorine in the fibers.

Tab. 14: Distribution of chlorine concentration in ppm

01/02: 1,220

03/04: 1,028

05/06: 9,508

Flap of an Officer’s Parade Sabretache

Fig. 5 and 6: Locations of measurement points for XRF and VIS on front and back.
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The XRF measurements yielded high values for chlorine and mercury and a moderate contamination with arsenic and lead. A notable result is the homogeneous distribution of the mercury between all the measurement points on the front side. A very slightly higher concentration was found in the red leather. The VIS measurement showed that the red leather was colored with cinnabar, which as far as we know today was a very rare and atypical red dye for leather.[52] Because this object, like the bicorne described above, belongs to the oldest part of the DHM collection dating from the early 19th century, we cannot rule out the possibility that it was treated with mercury chloride as a pesticide.

Tab. 15: Concentration range in ppm

Chlorine	4675.059
Mercury	105–362
Arsenic	16–245
Lead	287–1,433
Iron	not quantified
Copper	trace amount, not quantified
Zinc	trace amount, not quantified

The distribution of the lead concentration between the measurement points is judged to be fairly homogeneous. The relatively high value for lead at point 09/10 may be ascribable to a manufacturing technique. In this case we have a flaw in the metal embroidery which is completely missing in places so that the base fabric, a dark brown wool woven cloth, can be seen. A faint, light grey coating is visible on the wool fabric. A possible interpretation of that result involves an application that might have been part of the production, namely that white lead may have been used to chalk out the embroidery pattern. Similarly, the reading at point 03/04 which is located directly near the metal embroidery also shows a higher lead concentration that could have resulted from such a tracing.

Tab. 16: Distribution of lead concentration in ppm

01/02: 373
03/04: 674
05/06: –
07/08: 287
09/10: 1,433 (flaw in the metal embroidery)
11/12: 398
13/14: 373
15/16: 730

The arsenic concentration is relatively homogeneous, with small fluctuations that could be related to the consistency of the material at the respective measurement points. If we assume that arsenic was applied to this object as a biocide and dusted onto it as a powder, the slightly higher concentration at point 13/14 could be explained by the open structure of the silk embroidery at that point. On the other hand, the lower arsenic concentrations of 16 ppm (point 11/12) and 22 ppm (point 15/16) on the brown and red leather could be due to the relatively smooth surface structure of that material. The low arsenic concentration at point 09/10 could be explained by the loss of metal embroidery after the arsenic treatment.

Tab. 17: Distribution of arsenic concentration in ppm

01/02: 61
03/04: 75
05/06: –
07/08: 65
09/10: 20
11/12: 16
13/14: 245 (silk embroidery)
15/16: 22

In this object the chlorine concentration varies considerably for the different measurement points. The three lower values suggest a treatment with an organochlorine pesticide after 1945, despite the lack of documented proof. The medium concentration levels could be the result of a treatment with mercury chloride that was only applied to the exhibited side of the object at a time when its condition was more stable and the woolen fabric was less damaged. The extremely high chlorine concentration in the black silk embroidery could be due to the structure of the soft silk thread and the embroidery. Such structures will take up much more of an applied substance than a linen fabric. It is quite possible that over the course of the centuries several biocide applications and a few manufacture-related components accumulated to different degrees in the fibers, depending on the absorption capacity of the material.

The presence of mercury and chlorine could indicate mercuric chloride, which is mentioned in the literature as a biocide for the preservation of natural history collections.

Tab. 18: Distribution of mercury concentration in ppm

01/02: 237 (linen)
03/04: 263 (wool, linen)
05/06: –
07/08: 234 (linen)
09/10: 150 (embroidery flaw, wool)
11/12: 105 (leather, brown)
13/14: –
15/16: 362 (leather, red)

Fanion of a "Turco" Regiment of the French Army

Fig. 7: Locations of points for XRF and VIS measurements.
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This company flag of a North African ("Turco") regiment of the French army from 1870 belongs to the original Zeughaus collection. The red woolen cloth of the flag has motifs (of crescents and a Hand of Fatima) appliquéd in blue woolen cloth.

Of the four marker elements mercury, arsenic, lead and chlorine this flag was found to principally contain lead in concentrations ranging from 737 to 1909 ppm. Chlorine is found in low amounts at a few points. That is unusual in a woolen object that is vulnerable to infestation by insects and for which an earlier pesticide treatment would have been expected.

Tab. 19: Concentration range in ppm

Chlorine	162–388
Lead	737–1,909
Iron	not quantified
Copper	not quantified
Zinc	trace, not quantified
Tin	trace, not quantified

A possible reason for the application of lead may be the dyeing of the wool; this makes the results of the VIS spectroscopy particularly interesting. They indicate the presence of indigo dye in the blue cloth and carmine dye (cochineal) in the red cloth. A recipe for cochineal dyeing using lead hydroxide can be found in the literature from 1845: "Extract the cochineal with ether, then boil it in water and precipitate the carmine with so-called oxyhydrate of lead out of the aqueous solution."[53]

This suggests that lead could have been used for the dyeing of the red cloth. In the case of indigo dye, the combination with lead salts seems unlikely, since mordants were not needed for hot vat dyeing and the indigo cold vat required arsenic or orpiment.

A glance at the locations of the measurement points and the distribution of the lead concentration shows that it is relatively homogeneous with no significant difference between the red and blue cloth. That means that the dyeing method at least cannot be the sole reason for the presence of lead.

Tab. 20: Distribution of lead concentration in ppm

01/02: 780 (blue cloth)
03/04: 737 (blue cloth)
05/06: 1,285 (red cloth)
07/08: 1,350 (blue cloth)
09/10: 1,209 (red cloth)
11/12: 1,909 (red cloth)

Other possible sources of lead, such as vessels or pipes during the dyeing process, or car exhaust in the environment have also been considered. However, the concentrations detected in the objects are too high to permit such interpretations.

We consider the use of lead sugar as a biocide, both as an insecticide and a rodenticide to be a more plausible explanation. The manner in which the lead was applied – whether it was dissolved in the finishing liquor or used in powder form – remains a matter of speculation based on our current state of knowledge.

Rabbit Fur Cap

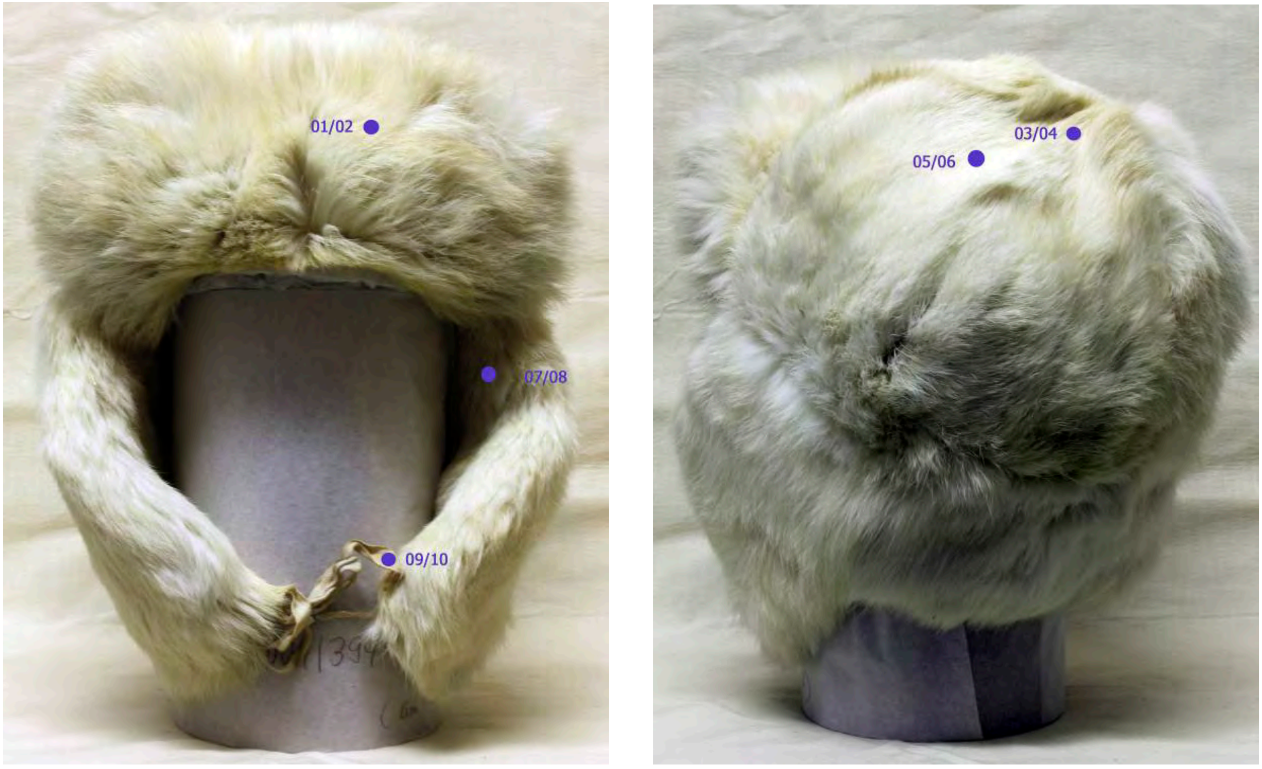

Fig. 8 and 9: Locations of measurement points for XRF on front and back.
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This fur hat from the 1980s is made of rabbit fur. The lining and the tie are made of regenerated cellulose. The results of the XRF measurements exhibit particularly high chlorine concentrations of 2,845 to 182,652 ppm. Although the chlorine concentrations in the fur are uniformly high, the values in the other materials deviate strongly from them. In the white tie we find an extremely high value while the blue lining has a relatively low chlorine concentration. These large variations lead us to believe that the measured values are due to manufacture-related substances.

Tab. 21: Concentration range in ppm

Chlorine	2,845–182,652
Iron	not quantified
Zinc	not quantified
Copper, Titanium	not quantified (in the blue lining)

The analysis only becomes interesting and interpretable once it is clear in what form the chlorine is present. In order to obtain that information a sample of the fur was studied using gas chromatography with mass spectrometry (GC-MS). The analysis showed slight, unquantifiable amounts of lindane, but otherwise none of the other volatile organic compounds that would be expected from organic pesticides. In other words, the chlorine markers point to inorganic chlorine compounds. As an inorganic pesticide, a chloroarsenate is a possibility, but can be eliminated due to the absence of arsenic. Instead it seems that the very high chlorine concentration in the fur and the tie of the once bright white cap can be attributed to a chlorine bleach.

Tab. 22: Distribution of chlorine concentration in ppm

01/02: 45,803 (fur)

03/04: 40,063 (fur)

05/06: 2,845 (interior lining)

07/08: 56,724 (fur)

09/10: 182,652 (tie)

Given the slight amount of lindane and since a contamination with lindane can be excluded both during the private ownership of the cap and during its time in the collection, we presume that the object was not treated with pesticides, but that the fur or the completed cap did come into contact with mothproofing agents before or during manufacture.

Boots of an Antarctic Researcher from East Germany

The situation is different for these fur boots worn by an East German researcher in an Antarctic expedition during the 1970s. In 2007 crystal deposits (efflorescence) were discovered on the object and identified as an insecticide using Fourier transform infrared spectroscopy (FTIR). The result was not investigated further, nor were the leather and felt studied with GC-MS.
The chlorine concentration was studied by XRF and yields differing amounts in the different materials. The levels in the fur are very high on both outside and inside, while they are lower in the leather and the felt sole. This result could be due to a manufacture-related application, but the chlorine may also have been applied unevenly at a later point once the object was part of a collection. The exact circumstances cannot be confirmed by the available measurement results.

Tab. 23: Distribution of chlorine concentration in ppm

01/02: 53,374 (fur)
03/04: 3,031 (leather)
05/06: 5,067 (wool felt)
07/08: 36,617 (fur - inside)
09/10: 52,245 (crystal efflorescence in the fur)
11/12: 28,514 (fur)
13/14: 1,806 (leather)
15/16: 3,133 (wool felt)

Fig. 10 and 11: Locations of points for XRF measurements.
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Boots from the East German women's Olympic team

Fig. 12: Locations of measurement points for XRF on inside and outside.
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The final example involves boots worn by the East German women's Olympic team during the 1968 Winter Games. The outside of the boots is made of synthetic imitation fur; the lining is lambskin.

The XRF measurements showed a small concentration of arsenic exclusively in the lambskin. Even so, the result is surprising for a textile object from this period. In general we have only detected arsenic in objects dating from no later than the end of the 19th century.

Tab. 24: Concentration range in ppm

Chlorine	152–24,413
Arsenic	6–34
Lead	30–293
Iron	not quantified
Zinc	not quantified

How can this result be interpreted with regard to potential biocide treatment? It is highly unlikely that in the 1960s fur used to make articles of clothing such as shoes would have been treated with arsenic. On the other hand, the concentration is so low that the possibility that the lambskin was prepared with arsenic can also be ruled out. Presumably it came into contact with scattered rodent poison during storage before the manufacture of the boots.

This case shows that even unsuspicious objects may be associated with a risk of contamination.

Tab. 25: Distribution of Arsenic Concentration in ppm

01/02: –
03/04: –
05/06: 34
07/08: 6
09/10: –
11/12: –

Concluding Remarks

Manufacturing-related ingredient or applied biocide? On the basis of selected examples we have undertaken to interpret the analytical results with reference to the application context. In some cases our explanations are inconclusive. More studies are needed to make these more concrete.

For many of the objects the analysis either has yet to be completed or has not yet been possible due to the very reduced availability of objects for the measurement of organic compounds.

Precisely these problems underscore how difficult it is to answer our initial question. However, in our view it is a crucial question, one which needs to be answered before a decision can be taken regarding a possible decontamination.

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Ina Stephan, Ute Schoknecht, Rudy Plarre

Introduction to biological means of testing the efficacy of biocides for the preservation of materials

In the natural cycle, materials are decomposed by both biotic and abiotic agents. Abiotic factors include, UV radiation, temperature, precipitation, abrasion and harmful gases, whereas the biotic factors include, bacteria, fungi, insects and rodents. Organisms are referred to as pests when they change or degrade the material contrary to the intention of the user.

Protection can range from simple measures, such as protection against the effects of weathering, to the use of chemical preservatives. The following article gives an insight into the use of chemicals (biocides) for material protection and the testing of their biological efficacy. Examples are given to show which tests for the assessment of the effectiveness of preservatives must be provided by the manufacturer before an approval is possible. What is not discussed in this text are the numerous studies with regard to toxicity and eco-toxicity, because the assessment of these properties is performed in the facilities of BfR (Federal Institute for risk assessment) and of the UBA (Federal Environment Agency).

There is a variety of chemical material protection products (general biocides) used in various fields. For clarity, these preservatives are divided, depending on their area of application, into groups (Product Types). An active substance may well be used in various types of end use either alone or in combination with others.

The biocidal products on the market are subdivided in the European Biocidal Product Regulation (BPR) into 4 main groups, and these in turn into a total of 23 Product Types. The Main Groups of biocidal product types (PT) as defined in Annex V of the Regulation, are: Disinfectants and general biocidal products (PT 1-5), preservatives (PT 6-13), pesticides (PT 14-19), other biocidal products (PT 20-23).

The authors believe, that the following products shown in Table 1 are of particular interest to restorers. The table also shows how many agents are currently approved by the BPR and how many agents are already notified, but for which the authorisation procedure has not been completed.

Active substances are often not individually applied in a protection product, but in combination with other active substances, e.g. to broaden the spectrum of activity to more fungal species (fungicides) or to introduce activity against algae (algicides). Furthermore, emulsifiers, stabilisers, etc., are often included to keep all of the components in a stable and applicable formulation. These preparations are then introduced into or onto the material to be protected. Again, it is possible that a biocidal formulation, e.g. in a cotton fabric, has a different interaction with a polyester textile that affects the accessibility of the active substances. This accessibility of the biocide (bioavailability) is very important for its effectiveness. The biocidal agent must come into contact with the organism it is required to affect. If the matrix to be protected covers or binds the biocide (e.g. a colour film) then, in the case of fungi on paint, they could grow uninhibited on the film, while the biocide is trapped within the paint film. To prevent this, the biocidal agent must reach the surface to protect the matrix, for example by diffusion or through conditions that lead to abrasion of the coloured pigments in the use phase. Under certain circumstances, it is also intended that biocidal active substances enter the water film that forms upon wetting of materials by dew or rain and be effective there.

Should the biocide migrate too quickly to the material's surface, it can be leached and rinsed off (e.g. by rainfall or washing). Should it move too slowly to the surface, the effectiveness may be incomplete. Usually, the amount of active compound that moves to the surface at the beginning of the use period is higher than in later time periods, when the total amount of available active agent is decreased. This means that the effectiveness of biocidal products may decrease over the course of exposure. Conversely, it may also take some time until the biocidal active ingredients reach the material's surface, and the biocidal activity can be intensified in the course of time, before decreasing in the long run. Since the binding of biocidal active ingredients and the mobility in the material

Tab. 1: Selected product types of the BPD

Field of us		**Producttype**	**Active substance approved acc. to BPR* / *being proceeded (2007)***
materials preservation	in- can-preservatives	6	- / *ca. 140*
	film preservatives	7	- / *ca. 90*
	wood preservatives	8	29 / *ca. 40*
	fibre, leather, rubber and polymerised materials preservatives	9	- / *ca. 130*
	masonry preservatives	10	- / *ca. 90*
also used in museums	rodenticides	14	14 / *14*
	insecticides, acaricides and products to control other arthropods	18	19 / *ca. 65*
	repellents and attractants	19	6 / *ca. 20*
	embalmment and taxidermy	22	- / *ca. 25*

* Stand Februar 2013

depends on their chemical and physical properties, the biocidal activity must always be considered in conjunction with the type of material in which it is employed. The manner of incorporation into the material is of importance for its bioavailability: the biocidal efficacy of the same active substance can differ whether, for example, in a synthetic fibre textile, the active substance is added by mixing it directly into the polymer yarn or by dipping the finished textile into an immersion bath or by spraying it onto the textile.

In the use phase of a biocidal product the long-term stability against UV radiation, temperature, other chemicals (eg cleaning agents) can also play an important role. These parameters are performed in so-called “stress tests” prior to the biological tests. These tests also simulate artificial accelerating aging of the biocides in the material.

In order to structure these complex issues, a two-tier process is applied.

In tier 1, the basic activity of a biocidal active substance is checked. However, testing at this stage must be done in a relevant matrix, in which the biocidal product is to be used later (e.g. cellulose-based textile, polyurethane, softwood). In tier 1, stress testing such as leaching, UV radiation, etc. is omitted. Test organisms may be rodents, insects (moths, beetles) and microorganisms (fungi, bacteria, algae). Generally, the test methodology is been developed in the European standardization bodies and will be valid throughout Europe.

When an active ingredient is proven to be effective and also satisfied the other conditions of admission, it is listed in Annex I of the Biocidal Products Regulation along with the parameters of its approval. In tier 2, the testing of a product is performed. At this stage, the stress tests mentioned above will be performed prior to the biological tests. The selection of the appropriate stress parameters will depend on the claim of the product.

The above-mentioned processes will be illustrated using the test of a biocidal product for protection against blue stain of wood. The biocidal product is part of a coating material which is applied in a defined amount to one surface of a wood specimen. This method intends to simulate a typical coating method, as applied e.g. for wood window frames. In order to artificially age the paint and accelerate the natural weathering process, the coated wood test specimens are mounted in an artificial weathering machine (Fig. 1). In such a cabinet the test specimens are exposed to defined and practically relevant amounts of UV radiation and irrigation. This is done according to an European-wide harmonised EU testing standard (EN 152:2011). Alternatively, an outdoor exposure over 26 weeks during the period between 1st March and the 31st October can be performed. Figure 1 shows a method for the artificial weathering of specimens. In the same way plastics, textiles or other materials could be artificially aged. However, it makes sense only when these materials are exposed to any such weathering in their later use phase.

Following the stress test in the weathering machine, the same specimens are sterilised and inoculated with spores of various fungi that cause so-called blue stain in wood (Fig. 2). The specimens are incubated for 6 weeks under conditions that are designed to provide the ideal growth conditions for blue stain fungi. In addition to the coated wood specimens, uncoated wood specimens are used in the test to detect the potential for colonisation and discolouration of the wood. The untreated specimens are employed to validate the experimental procedure. Such controls are an important part of any microbiological efficacy test for biocides.

After incubation, the surface of the paint is evaluated for discolouration caused by blue stain fungi (Fig. 3). A blotchy appearance may indicate that the biocidal product is not evenly distributed in the coating. For further evaluation the wood specimens are divided into three, cross sectional parts. The extent of staining of the cross-sectional areas of the middle piece of wood is documented by noting how close the blue stain fungi grew towards the biocide containing coating (Fig. 4).

The efficacy testing of preservatives against blue stain serves as an example to demonstrate product testing. The general rule is that all label claims of biocidal products must be confirmed by scientifically generated data. Not all materials are susceptible to damage by living systems therefore this approach encourages the principle that only materials that need to be protected are protected. Benefits and risks associated with use of a biocidal product to mankind and the environment must be balanced. In this process, the effectiveness of a biocide is absolutely necessary, but is only one factor in the approval of a biocide.

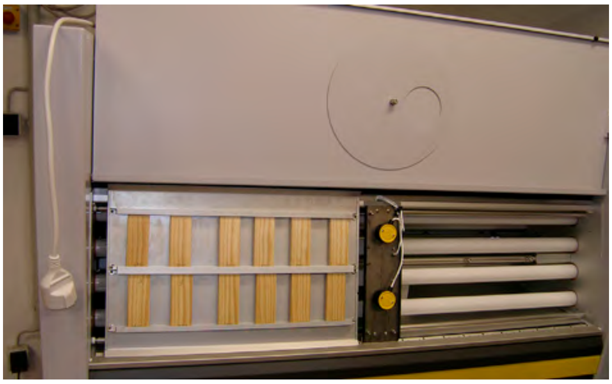

Fig. 1: Opened weathering machine ("QUV"). On the left half the test specimens are installed in the holder to be turned over, so that the test specimens are facing the fluorescent tubes and the irrigation nozzles.

DIN EN 152 Wood preservatives - Determination of the protective effectiveness of a preservative treatment against blue stain - Laboratory method ; German version EN 152:2011

Fig. 2: Left: wood specimens ready to be inoculated with fungal spores of blue stain fungi and to be incubated on water holding granules in the experimental vessel; right: obtaining a fungal spore suspension by filtration of an aqueous extract of sporulating fungal cultures.

Link to the Federal Institute for Occupational Safety and Health : http://www.baua.de/de/Chemikaliengesetz-Biozidverfahren/Rechtstexte/Re chtstexte.html

Fig. 3 + 4: wood specimen after controlled incubation with blue stain fungi in the laboratory. Left column: untreated wood, middle and right columns : Painted wood surfaces with biocides of different effectiveness.

Example cross sections of the wood specimens after controlled incubation with blue stain fungi in the laboratory. Left column: untreated wood, staining over almost the entire cross-section, middle and right columns: wood painted with biocide containing top-coat showing different effectiveness in depth.

website of the European Chemicals Agency : http://ec.europa.eu/environment/biocides/

Dagmar Holthenrich, Vera Ritz

Health Risk Assessment of Biocides Used to Maintain Exhibits in Museums, Collections and Archives

Biocides are chemical or biological substances that must be effective in controlling damaging organisms. They can also be harmful to humans and the environment. The types of products listed in Table 1, among others, play a role in the maintenance of exhibits in museums, collections and archives.

Since 1998 there have been European legal regulations set in accordance with Directive 98/8/EG[1]. This was superseded on 1 September 2013 by Regulation (EU) Nr. 528/2012[2]. They are valid for new biocidal active substances and "older" active substances marketed in biocidal products before 5 May 2000. In a first step, the biocidal active substances and a representative formulation are tested to determine the degree of unacceptable threat they pose to consumers, the environment and workers, and if they are sufficiently effective. When a biocidal active substance is approved, the biocidal product goes through a second step – a authorisation procedure. At this stage as well, objectives such as effectiveness and consumer, worker and environmental safety are the focus.

At the start of the process for an active substance, industry must name all the active substances in order for them to be listed and authorised for different types of products.

Active substances that are used in wood preservatives, insecticides and rodenticides are first tested by EU member states. A few biocidal products for these product types have already been authorised.

Various federal authorities are integrated in the legal procedures for biocides in Germany. The health risk assessment takes place through cooperation between the Federal Institute for Risk Assessment *(Bundesinstitut für Risikobewertung (BfR)*, and the Federal Institute for Occupational Safety and Health *(Bundesanstalt für Arbeitsschutz und Arbeitsmedizin (BAuA)*. The *BfR* carries out a risk assessment for substances and products and evaluates the threat they pose to consumers. The *BAuA* has the responsibility for assessing risks in the workplace.

Approval for Active Substances

The first step of the EU-wide approval procedure for active substances requires the applicant to submit a comprehensive set of data, or dossier, to one of the EU member states – the reporting EU member state. Applicants are predominantly manufacturers of biocidal substances. The dossier submitted contains, among other things, information about toxicity, user exposure, and exposure of the general public with respect to a sample product, as well as data on effectiveness and environmental compatibility. The reporting member state then tests the data in detail and evaluates it. The resulting draft assessment report contains opinions, including a recommendation for approval or non-approval based on identified risks. This is sent to the European Commission. Active substances that are assessed and found to have particularly critical

Tab. 1: Types of Products that Play a Role in the Restoration and Maintenance of Exhibit Items as Set Down in EU Regulation Nr. 528/2012

Main Group 2: Preservatives	Product type 8	Wood preservatives
	Product type 9	Fibres, leather, rubber and polymerised materials preservatives
	Product type 10	Construction material preservatives
Main Group 3: Pest control	Product type 18	Insecticides, acaricides and products to control other arthropods
Main Group 4: Other biocidal products	Product type 22	Embalming and taxidermist fluids

toxicological characteristics, such as reproductive toxicity or carcinogenicity, cannot, as a rule, be approved. This is followed by a subsequent peer review which is carried out by the member states in order to achieve a coordinated opinion. The expert vote on the European decision for approval or non-approval is then registered with the Standing Committee on Biocidal Products.

The dossier that must be submitted by the applicant for health evaluation of the active substance consists of data gathered in animal testing and studies of acute toxicity, including skin and eye irritation, skin sensitisation, and also data on repeated dose toxicity, reproductive and developmental toxicity, mutagenicity, carcinogenicity, chronic toxicity and neurotoxicity, as well as medical data (case reports, studies, poisonings, summaries of occupational medical investigations) information about absorption through the skin, and after oral ingestion or inhalation. Information about acute toxicity, including skin and eye irritation and skin sensitisation is to be submitted for the sample product. These can be results of animal studies or calculations based on the concentration of active substance in the product. Furthermore, the applicant must submit information about application of the sample product and the exposure that can result to users and the general public.

The reporting member state assess the studies and information and from these derives limits for comparison with expected exposure for short and moderate periods as well as chronic exposure.

The responsible authority also asses expected exposure for users (consumers and employees) based on the data submitted.

While oral intake can play a role for the consumer and the general public (e.g. through residues in food), in the workplace intake of the chemicals being considered predominantly takes place via the skin (dermal) and respiratory tract (inhalation).

The properties of the substance and application can effect various areas of the skin and/or parts of the respiratory tract. Therefore, for example, the hands could potentially be affected during decanting to mix solutions, whereas during spraying, it must be assumed that there will be contact with large areas of the body. In addition to dermal exposure, exposure through inhalation must also be evaluated. If the chemical is also volatile, inhalation of vapours must be considered as well. If the application involves spraying, exposure to aerosols must also be evaluated. The level of exposure is preferably determined using available measurement data for dermal exposure and exposure through inhalation. If there are no measurement data, a range of exposure models are available.

During the subsequent risk assessment, the level of exposure is compared to the toxicological limit that fits each duration of exposure (see Fig. 1). If exposure is under the limit, then from a health standpoint, approval may be issued. If exposure exceeds this limit, then tests are first carried out to see if risk reduction measures such as technical ventilation or personal protective equipment in the workplace reduces exposure to below the limit. If this is not the case, then safe use is not guaranteed and approval is denied.

A list of approved active substances can be found on the website of the REACH-CLP Biocide Helpdesk.[4]

Authorisation Process for Biocidal Products

After successful approval of an active substance, a product containing the active substance must be authorised within a certain deadline in the EU member states where its marketing is planned in order for it to be used for the first time in the case of a new active substance, and for its continued use in the case of an old active substance.

The applicant must submit information about the product for product authorisation. Data from the ac-

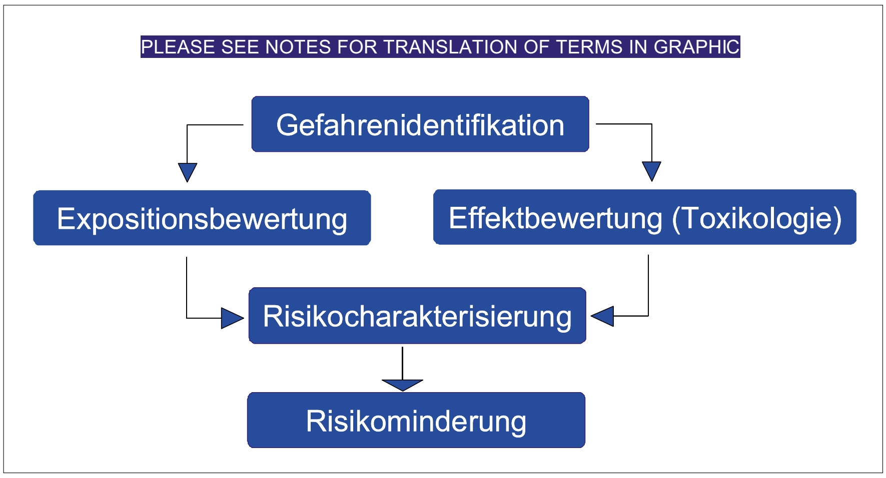

Fig. 1: Risk Assessment and Risk Management (Risk Reduction). Simplified diagram as presented by Van Leeuwen (1995).

tive substance approval process are also consulted for the active substances used in the product. The *BfR* also carries out the consumer health evaluation for product authorisation. With respect to occupational safety, the *BAuA* formulates risk reduction measures for identified risks. These can applied to the product or specific types of applications. Furthermore, the *BAuA* sets the conditions under which the product can be safely used in the workplace. The holder of the authorisation (license holder) must place these conditions of use on the label or in directions for people using the product on the job. With respect to the use of biocidal products that are used in the restoration and maintenance of exhibition pieces, the activity of the user (e.g. restorer) is also assessed. In this case, the direct contact with the chemical and also the exposure resulting from the treated object must be taken into consideration. This can effect museum personnel and visitors as well.

For various reasons, not all the products that file for authorisation receive it. As a result, at the end of the authorisation process, not all the biocide products on the market at the time will be available.

Because the evaluation of active ingredients has yet to be concluded, there are predominantly products on the market today that have yet to be tested through the authorisation procedure. But professional users are nevertheless protected if they adhere to the rules set down in the regulations for hazardous substances[4]. Whether a product is authorised can be recognised by the authorisation number on the label. If there is a registration number on the label made up of a letter (N-) and a five-digit number, then the product is a biocide that has been registered on the German market but has yet to be evaluated during an authorisation process. A current list of the biocidal products that have been authorised in Germany up to now can be found on the homepage of the *BAuA*[5]. A directory of the products registered in Germany can also be found there[6].

"Contaminating residue" caused by active substances that are not (no longer) approved

Because the evaluation process for biocides is not yet concluded, many active substances have not been conclusively evaluated and authorised. Furthermore, it is precisely through contact with exhibit items that exposure to non-approved active substances or persistent "contamination" with, for example, biocides containing organophosphates or heavy metals is to be expected. Because these products have in part not been used for decades, as a rule there is no acceptable toxicological data for deriving limits, which precludes the usual risk assessment carried out during the biocide procedure. If it is suspected that "contaminating residues" with hazardous properties could be encountered during handling of the exhibit items, then a corresponding hazard assessment is to be carried out in accordance with Paragraph 6 of the regulations for hazardous substances[6].

The Technical Rule for Hazardous Substances (TRGS) 400: Risk assessment for activities involving hazardous substances *(Gefährdungsbeurteilung für Tätigkeiten mit Gefahrstoffen)*, describes in detail the procedures for gathering information and risk assessment. Supplemental to that are among others, the Technical Rule for Hazardous Substances *(TRGS)* 401: "Risks resulting from skin contact – identification, assessment, measures" *(Gefährdung durch Hautkontakt Ermittlung – Beurteilung – Maßnahmen)*, and TRGS 402: "Identification and assessment of the risks from activities involving hazardous substances: inhalation exposure" *(Ermitteln und Beurteilen der Gefährdungen bei Tätigkeiten mit Gefahrstoffen: Inhalative Exposition*), to be considered[7]. Valuable support can also be found in the Technical Rule for Hazardous Substances (TRGS) 524: "Protective measures for activities in contaminated areas" *(Schutzmaßnahmen bei Tätigkeiten in kontaminierten Bereichen)* when renovating buildings that may be contaminated with remnants of hazardous materials[7].

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http://www.baua.de/de/Themen-von-A-Z/Gefahrstoffe/Rechtstexte/Gefahrstoffverordnung.html (in German)
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Oliver Hahn

Blessing and Curse: Biocides, a Concluding View

Pest infestation of art and cultural goods remains a great challenge. Historical pest control, which has tried since the 18th century to prevent infestation by applying toxic agents, has resulted in many problems today. The application of toxic substances in the materials has made the simply handling of contaminated cultural goods impossible.

The agents used comprise a broad spectrum of different substances. Arsenic, mercury, and lead compounds were used to fight pests, as were organochloride compounds (DDT, PCP, Lindane, Eulan, methoxychlor, permethrin), triphenylmethane, sulfonamide derivates, diphenylurea derivates, and phosphonium salts. When which agents were actually used in what amounts is seldom documented. This means that the health risks for employees and the possible damage to the artworks cannot be assessed with the current state of knowledge. Specially adjusted investigative procedures document that several generations of biocidal agents were often used on the same objects.

The papers presented in this publication underscore that dealing with these legacy burdens is a collective task that requires transdisciplinary collaboration among restorers, curators, natural scientists, and physicians. The example from the German Historical Museum, alone, impressively documents here that only transparent and open cooperation holds out prospects for guidelines and suitable catalogs of measures to be taken to avoid health risks, but also to lastingly preserve art and cultural goods. Here, transparent and open cooperation means critical discussion among restorers and curators, realistic assessment of the possibilities and limitations of natural-scientific analysis procedures, and the health and occupation-medical evaluation of the biocidal agents.

The catalog of questions raised by the presence of toxic compounds in the objects in many museums' collections is diverse. Beyond the questions of "what" and "how much" was used, preventive health protection is a much-discussed topic. Here, of course, the assessment of risk potential is especially important: are we dealing with low-volatile compounds that do not contaminate the room air much, but burden dusts and the objects themselves? Were more volatile substances employed, for example naphthalene or Lindane, which can sometimes be detected in substantial amounts in the room air? Should the biocides that were used be removed from the objects, since they pose a danger not only for people and the environment, but also for the objects themselves? What is the suitable, i.e., the most effective and at the same time least damaging method of decontamination? And what happens in the end with the decontaminated objects?

Dealing responsibly with cultural goods contaminated with toxins demands a great deal of collective work, much time, and thus much money. Where funds are short, the latter point is very important. This often limiting factor, however, must not lead to hushing up the problem and withdrawing the burdened objects from public access. For this reason, the pilot study of the textile collection at the German Historical Museum opens the path that other collections should follow.