DOI: 1234567890
Published: 1 November 2018

The use of cyclododecane in Swiss archaeological contexts

Frédérique-Sophie Tissier

Cyclododecane (CDD) has been used since 2004 by the Archaeological Service of the Canton of Bern, Switzerland in a wide range of situations. This article summarises various practical experiences from our institution in the field as well as in the laboratory. Experiences during excavations in Basel led to the development of the 'sandwich technique' for block-lifting fragile artefacts, described in this paper. The long-term storage of Roman painted wall plaster lifted with CDD brought compatibility problems to light, in particular with ethyl silicate. Investigating the potential contamination by CDD of samples for C^{14} dating has also been a topic of concern, as has the residue question, which has been addressed in two graduate-level projects through FTIR, GC–MS and gravimetric methods. Health and safety issues were investigated with exposure measurements that reproduced work scenarios, for example in a trench or under a fume hood depending on the application method. Finally, a flow chart for decision-making is provided as a tool to help determine whether CDD is suitable for block-lifting, especially when further treatment is required.

1 Introduction

In 2005, I heard about the conservation material cyclododecane (CDD) for the first time while undertaking an internship in archaeological restoration on the island of Cyprus. My supervisor, who was also the head of a conservation laboratory in Switzerland (Christoph Rogalla von Bieberstein), explained the properties of CDD. He also suggested that further research about its uses in archaeology should be the subject of a Masters degree. One year later I was enrolled in the Masters programme at the University of Paris 1-La Sorbonne, with a focus on the application of CDD for temporary consolidation of archaeological materials in the field. In 2008, another student from the Conservation School ARC in La Chaux-de-Fonds, Switzerland, started to work on CDD, with an emphasis on the sublimation process, on residues and on radiocarbon dating. This article presents a critical review of the results from projects carried out at the Archaeological Service of the Canton of Bern (ASCB), based on eight years of experience with the material. The following examples demonstrate some practical aspects of CDD use in the field and the laboratory.

2 The 'sandwich technique'

Lifting an artefact in a block is often a heavy responsibility for the conservator. In cases where one or more objects are too fragile to be lifted by hand, or when it is important to preserve the relationships between several objects, consolidation in a block is necessary for safe transportation to a conservation lab, where optimal conditions for excavation can ensure the preservation of information. The most common technique is lifting with plaster of Paris bandages since they are simple to use, non-toxic and inexpensive.

Even so, this technique is not applicable in every situation: the Celtic grave no. 15 at the Gasfabrik site in Basel, Switzerland is one example where bandages could not be used. Discovered in 2006, the grave of a four-year-old child was located amongst other graves in a zone of gravel and sand (Figure 1). The grave goods, consisting mainly of an iron chain, bronze fibulae and a glass bracelet, were too fragile and scattered to be lifted with plaster bandages. The Basel archaeologists needed a new technique for block-lifting the artefacts – not only for this grave but also for others at the site. They contacted the ASCB, who came to the site to test block-lifting with CDD. The first step consisted of isolating the area with aluminium foil since CDD does not adhere directly to damp soil. Molten CDD was then applied with a polyethylene pipette as a protection layer to the most delicate objects like the glass bracelet. A first layer of CDD was sprayed over the surface of the soil block with a spray gun, applied at a distance of about 5 cm, with 1 bar of pressure at 80 °C (see Hangleiter *et al.* 1995) (Figure 2). Bands of washed cotton gauze were laid over the first layer of CDD and

Figure 1 Celtic settlement at Basel-Gasfabrik, Switzerland, 2006. Grave goods in situ: glass arm ring, belt chain, bronze brooches. Photo courtesy of the Archäologischen Bodenforschung Basel-Stadt.

a second layer was sprayed on, serving both as a consolidant and reinforcement for the cotton gauze. It was important to use washed fabric in order to avoid shrinkage. Finally, a synthetic plaster (Ebacryl L-1/EM-1) reinforced with fibreglass was used to create a rigid cover. It was then possible to dig around the block and use the more traditional plaster bands to secure the walls, so the block could be lifted and turned upside down. The technique of using CDD sandwiched with the cotton gauze allowed the artefacts to be successfully transported to the laboratory. After this we acquired X-ray pictures and CT scan images, before excavating the block. After studying the assemblage, the archaeologists were able to state that the set of jewellery had been wrapped in cloth and placed on the chest of the little girl, and gained a better understanding of Celtic funerary practices (Spichtig and Tissier 2008: 30–33).

Following this first successful intervention, a workbox was developed for stabilising and lifting of small soil blocks on site (Figure 3). The box contains a heating plate with a safety screen, a lidded pan for heating CDD, personal protective equipment,

Figure 2 Celtic settlement at Basel-Gasfabrik, Switzerland, 2006. First application of molten cyclododecane with a spray gun, for stabilisation before the block lifting of the grave goods. Photo courtesy of the Archäologischen Bodenforschung Basel-Stadt.

rolls of washed cotton gauze and polyethylene pipettes. The plastic pipettes were no longer included in the workbox following the publication of Jägers and Sicken (2012). This article identifies the contaminants on textiles as polyolefin residues linked to the use of thermoplastic polyethylene pipettes. The CDD workbox, either with or without the spray gun, has proved its worth in the field, particularly in cases where other methods for consolidation were not an option.

3 Temporary … up to what point? Consolidation of painted wall plaster for medium-term storage

Excavated archaeological materials should be stored in a manner that conserves their information potential until it can be studied. The following example raises questions about the durability and compatibility of CDD in these cases – since the time between excavation and research can be as long as 15 years at the ASCB. In 2008 an assemblage of Roman painted wall plaster was lifted with CDD using the 'sandwich technique'. At the time the material was stored, it was not known when the study would take place, but it was thought possibly within two years following excavation. The fragments were stored face down in sealed boxes. On each block, the site coordinates, inventory numbers and orientation were written in indelible marker (directly onto the CDD). It was six years later, at the end of 2014, when the decision was made

Figure 3 Workbox for small block-lifting on site. Photo: Archaeological Service of the Canton of Bern (ASCB).

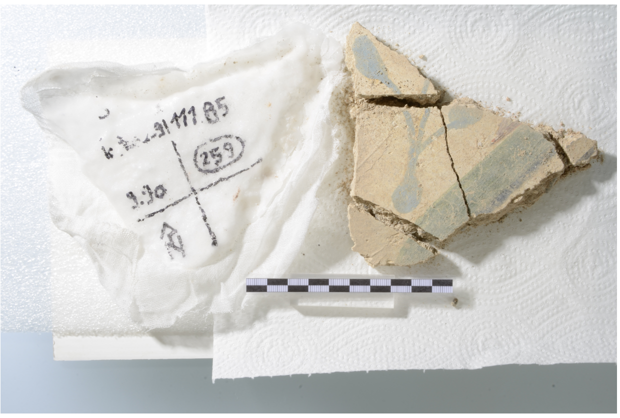

Figure 4 Wall plaster fragments, lifted with cyclododecane on cotton gauze. Six years after the lifting, the inscriptions had become less readable through CDD sublimation. Photo: ASCB.

to bring the fragments out of storage for research. Unfortunately, the inscriptions had become less readable through sublimation of the CDD (Figure 4). The CDD was removed mechanically, with the help of hot air guns to accelerate sublimation locally. The overall result was otherwise positive since the temporary consolidation maintained the fragments in position for many years.

At the same time, a test of permanent consolidation raised an unexpected issue. I had wanted to examine empirically what interactions could possibly happen between wall plaster fragments lifted with CDD and a specific consolidation medium. This was

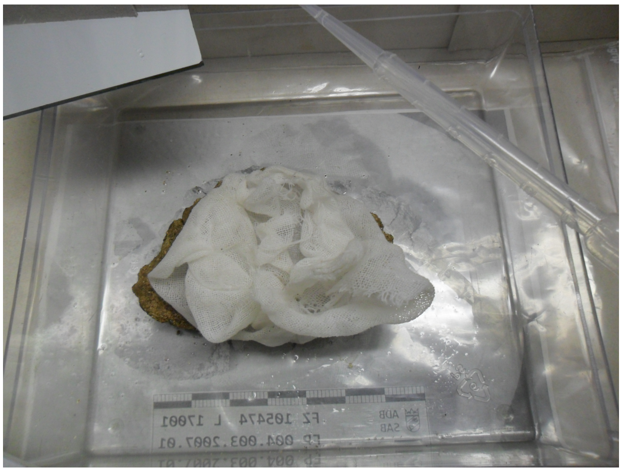

Figure 5 Wall plaster fragments, lifted with cyclododecane on cotton gauze, during impregnation with an ethyl silicate. Photo: ASCB.

tested by samples of the plaster that had been fully impregnated with an ethyl silicate (KSE 300, Remmers) (Figure 5). The cotton gauze soaked in CDD was easily detached after impregnation, although it had been firmly adhered to the surface with CDD before impregnation. These observations were confirmed by placing a solid piece of CDD (1 cm × 1 cm × 3 mm) in a receptacle filled with KSE 300. After 30 minutes, the CDD had passed completely into the solution. The question of the interaction between the CDD and the ethyl silicate warrants further examination in order to anticipate consequences for the treated materials. A fundamental question is to find out if a temporary consolidation with CDD could prevent or render the permanent consolidation with ethyl silicate less effective. Decisions about applying CDD should take into account the other materials used for later treatments. The conserved material should also be regularly examined to make sure that the CDD is performing as expected and that the associated information are still visible and accessible.

4 Radiocarbon dating and residues

In archaeology, it is very important that on-site conservation does not contaminate samples destined for carbon dating C^{14} processes. As CDD is a hydrocarbon, its carbon element content could possibly compromise the dating.

As part of her Master's degree, Stefanie Bruhin conducted tests at the Institute of Physics, University of Bern to examine whether CDD could falsify the results obtained from C^{14} dating. Three samples

Figure 6 Jegenstorf, Zuzwilstrasse, Switzerland, 2010. Fired clay mould for making a bronze bell. First application of molten cyclododecane with a spray gun, for stabilisation before block-lifting. Photo: ASCB.

of wood that had already been dated were covered with melted CDD. Once sublimation was complete, the wood was retested by conventional radiocarbon methods [1]. The results proved to be surprising: the date provided by the second test was within the range of the first results (Bruhin *et al.* 2008: 104–113). If CDD had had an impact on dating, according to the original amount on the sample, the age difference could have reached about one hundred years (Bruhin *et al.* 2008: 111): 'Assuming that the samples treated with preservative [...] had been contaminated with 1% CDAN [cyclododecane], so the samples' ages would have been 80 years too high. However, this is obviously not the case' (Bruhin 2008).

In 2010, a second artefact, a fired clay mould for making a bronze bell, was used for a further series of tests and confirmed that the CDD had little effect on radiocarbon dating (Figure 6). The base of the mould had been consolidated with CDD; one associated charcoal sample had been taken before the consolidation, a second afterwards. Both were tested using accelerator mass spectrometry (AMS), which gave comparable results (925 BP[2], ± 35 with CDD and 895 BP, ± 35 without CDD). These results were consistent with those of an earlier study conducted in the United States by a team of researchers and conservators, also using AMS (Pohl *et al.* 2009).

Many authors have treated the subject of residues (e.g. Riedl and Hilbert 1998; Rowe and Rozeik 2008). Two graduate-level projects at the ASCB have furthered such studies. The first project dealt with samples of ceramic, bone, metal and cardboard that were treated with CDD and analysed by Fourier-transform infrared spectroscopy (FTIR) and gas chromatography with mass spectrometry (GC–MS)[3] after CDD sublimation. The types of samples were diversified in order to obtain a representative survey of porous materials that had been treated with two CDD application methods (melted and vaporised), and to investigate the possible relationships between porosity and presence or absence of residues. Of twelve samples, ten showed residues of CDD, no matter the application method. Among the two samples without residue, one could not be investigated because it could have damage the GC injector. The last sample, a flowerpot fragment, showed no residue after two extractions (with benzene and hexane), probably because of its low porosity. In the second project, Stefanie Bruhin examined residues of melted CDD from ceramic, glass, iron, bone and textile samples after sublimation controlled by gravimetric methods (that is, by monitoring very small changes in weight). She first demonstrated the purity of the CDD from two different suppliers[4] by GC and GC–MS. The analyses showed residues of non-sublimated cyclododecane, but also cyclododecanone, dodecanol and tetradecanol. These may be secondary products from the synthesis of CDD, as is suggested by comparable studies (Caspi and Kaplan 2001: 119–122). In both studies, residues were found after complete sublimation. These residues represented often no more than 0.01% of the initial mass of the binding media. But how significant is that? There remains a wide scope for further testing, in order to understand the possible impact of these residues on every type of material, in combination with their associated treatments.

5 Health and occupational safety

Following the completion of her Master's degree, Stefanie Bruhin conducted tests in 2009 on health

1 Method based on radioactivity measurements, one being called the 'Gas Proportional Counting' method.
2 BP indicates before present (1950).
3 At the research laboratory of the Swiss National Museums (see Tissier 2007: 72–76).
4 Merck and Kremer Pigmente; more details in Bruhin *et al.* (2008: 94–103).

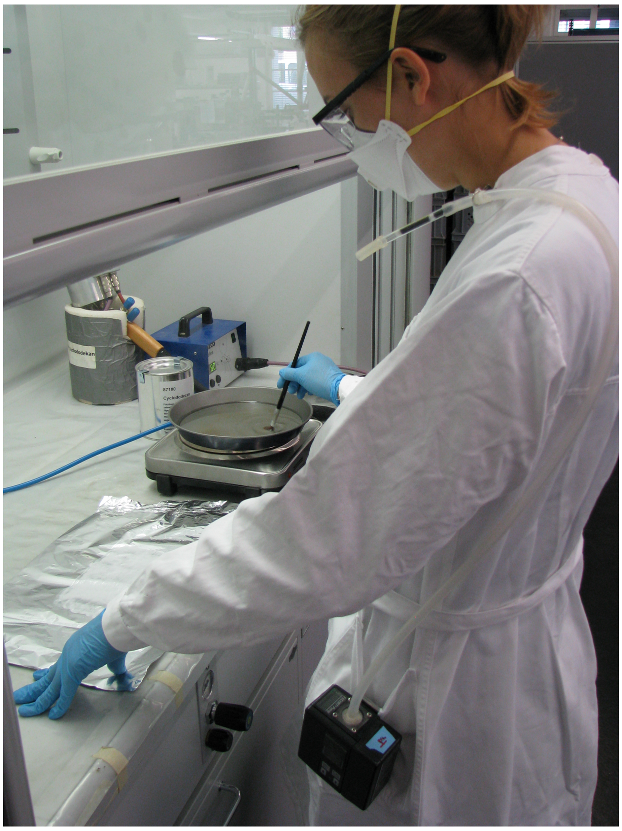

Figure 7 Workplace exposure measurements for molten cyclododecane applied by brush under an operative exhaust hood. Photo: ASCB.

and workplace safety. In collaboration with the Institute for Work and Health, Lausanne, the exposure levels at workstations were measured in the laboratory of the ASCB (Vernez *et al.* 2011). The results helped to reveal exposure patterns for CDD as a function of the application methods (spray gun, melted, under an exhaust hood or in the open air) (Figure 7).

The samples were collected with charcoal sorbent tubes fixed near the respiratory tract of the workstation operator. The CDD concentrations were then determined by gas chromatography coupled with a flame ionisation detector (GC–FID) (Table 1). The heaviest concentrations were measured during use of the spray gun, particularly in a trench without special ventilation – the same situation encountered in fieldwork. The tests clearly demonstrated that ventilation at the source greatly reduces CDD emissions and that use in the open air does not guarantee reduced exposure. The problem of a lack of official exposure limits for CDD means that through the tests and concentration measurements obtained, it still is not possible to determine the precise risk incurred by the operator. However, on the basis of previous work on the persistence and bioaccumulation of this product (European Chemical Agency (ECHA) 2008), and in accordance with precautionary measures, we prefer to always use personal protective equipment (nitrile gloves, solvent respirators and safety glasses) and, if possible, air ventilation during application and sublimation.

6 Tool for decision-making

As shown by these tests, the use of CDD is not without risk. In order to strictly control how and when conservation with CDD should be considered, we have developed a decision-making chart (Figure 8). Certain issues should be clarified before any use of CDD. Is it really necessary or are there good alternatives? Is the substrate sensitive to non-polar solvents, and in particular to the family of hydrocarbons that CDD exhibits during its liquid phase? Is the substrate sensitive to heat? What types of analysis are planned for the artefact? What conservation and restoration treatments will be used afterwards? What possible interactions are likely to occur? The duration of time the CDD remains in contact with the object must also be envisioned beforehand, so that regular monitoring can be scheduled. Similarly, before any intervention, the removal method for the CDD must be chosen: spontaneous or accelerated sublimation? Is ventilation available as well as personal protective equipment? Are all of these considerations within the allotted budget for the project? And is it ethically correct to use a product where we do not have a complete understanding of its human and environmental toxicity?

7 Conclusion

Eight years after the intervention at Basel, what could have been done differently? This sort of methodological questioning is always pertinent for improving conservation work. Since 2006, our equipment in the field has evolved to become more efficient. Some changes made in the practice of CDD consolidation are the result of being better informed about some of its possible interactions (for example with the polyethylene pipettes). Past experiences allow better planning strategies and the ability to anticipate certain consequences (e.g. the incompatibility of identification tags made with marker ink on CDD covered surfaces).

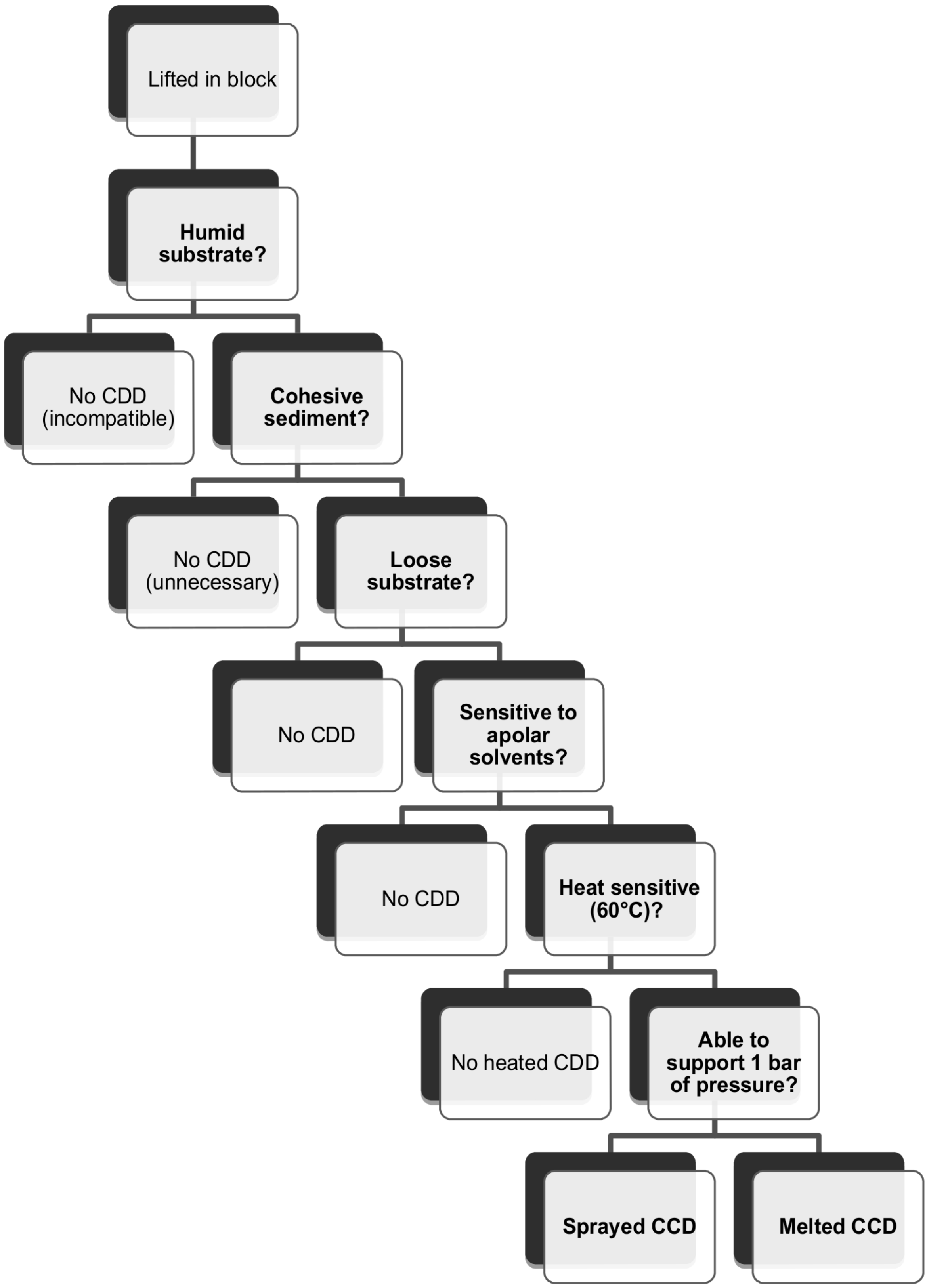

Figure 8 Flow chart for decision making: preliminary questions for the use of CDD. Figure: ASCB.

Technique	Ventilation	Concentration range (mg/m^3)	Average concentration (mg/m^3)	Maximum concentration (mg/m^3)
CDD sprayed with gun	Hood operating	0.06 – 1.6	0.75	1.6
CDD melted, applied by brush	Hood operating	0.53 – 1.0	0.85	1.0
CDD melted, applied by brush	Hood not operating	0.55 – 40.6	15.5	40.6
CDD sprayed with gun on vertical surface	Open air	12.7 – 24.4	19.5	24.4
CDD melted, applied by brush	Open air	10.2 – 40.4	23.3	40.4
CDD sprayed with gun	Open air	12.7 – 24.4	24.2	24.4
CDD sprayed with spray gun in a trench	Open air	30.9 – 74.4	53.9	74.4

Table 1 Exposure levels to CDD during typical activities. Source: Vernez *et al.* (2011)

These experiences have also excluded certain risks, such as the distortion of radiocarbon dating. Yet many questions about the use of CDD remain unanswered, particularly those concerning toxicity and occupational health risks, as well as its compatibility with other conservation materials. The ethical dilemma has been resolved by choosing to use this product when there is no better option, but with a preliminary reflection on the whole process, with adapted protective measures and by sharing our experiences with the community of conservators and researchers.

Biography

Frédérique-Sophie Tissier graduated from the Université de Paris 1 La Sorbonne (France) in 2002 with a Bachelor of Archaeology and a Master in Conservation-Restoration of Cultural Goods (2007), specialising in archaeological objects. She joined the Archaeological Service of the Canton of Bern (Switzerland), where she experimented with cyclododecane in the field and in the laboratory. In 2008 she became chief of the Mineral Objects Conservation Section, and has since taught in situ conservation to the students of the Haute École Arc in Neuchâtel (Switzerland).

Email: frederique.tissier@erz.be.ch

References

Bruhin, S., Eyermann, T., Jeberien, A., Rogalla von Biederstein, C. and Tissier, F.S. (2008), 'Der Einsatz von Cyclododecan zur archäologischen Fundbergung: Möglichkeiten, Grenzen und Forschungsbedarf (The application of cyclododecane for rescuing archaeological finds: prospects, limitations and the need for further research)', *Restaurierung und Archäologie* **1**, pp. 53–67. German with German, English, French summaries.

Bruhin, S. (2008), Personal communication. Radiocarbon-Labor, Physics Institute, University of Bern.

Caspi, S. and Kaplan, E. (2001), 'Dilemmas in transporting unstable ceramics: a look at cyclododecane', *American Institute for Conservation, Objects Specialty Group Postprints* **8**, pp. 116–135.

European Chemical Agency (ECHA) (2008), 'Annex xv dossier: cyclododecane', URL `http://echa.europa.eu/documents/10162/13640/svhc_axvrep_france_pbt_cyclododecane_20083006_en.pdf`.

Hangleiter, H.M., Jägers, E. and Jägers, E. (1995), 'Flüchtige Bindemittel – Teil 1: Anwendungen, Teil 2: Materialien und Materialeigenschaften', *Zeitschrift für Kunsttechnologie und Konservierung* **9**(2), pp. 385–392.

Jägers, E. and Sicken, A. (2012), 'Unerwünschte Rückstände: Neue Erkenntnisse zur Behandlung textiler Oberflächen mit Cyclododecan', *Restauro* **6**, pp. 36–38.

Pohl, C.M., Hodgins, G., Beaubien, H.F. and Speakman, R.J. (2009), 'The effect of cyclododecane on carbon-14 dating of archaeological materials', *JAIC* **48**, pp. 223–233.

Riedl, N. and Hilbert, G. (1998), 'Cyclododecan im Putzgefüge: Materialeigenschaften und Konsequenzen für die Anwendung in der Restaurierung', *Restauro* **104**, pp. 494–499.

Rowe, S. and Rozeik, C. (2008), 'The uses of cyclododecane in conservation', *Reviews in Conservation* **9**, pp. 17–31.

Spichtig, N. and Tissier, F.S. (2008), 'Blockbergung mittels Cyclododekan am Beispiel eines latènezeitlichen Grabes von Basel-Gasfabrik', *Archéologie Suisse* **31**(4).

Tissier, F.S. (2007), *Le cyclododécane en conservation-restauration d'objets archéologiques*, Master's thesis, Université Paris 1-La Sorbonne.

Vernez, D., Wognin, B., Tomicic, C., Plateel, G., Charrière, N. and Bruhin, S. (2011), 'Cyclododecane exposure in the field of conservation and restoration of art objects', *International Archives of Occupational and Environmental Health* **84**(4), pp. 371–374.