Cyclododecane Applied on Archaeological Materials: Sublimation Rate Increase by Mean of Fume Cupboard

Corinna L. KOCH DANDOLO
Lugano, SWIZERLAND

ABSTRACT

Cyclododecane (CCD) is used as a temporary consolidation product by the Conservation Department of JIAA-Japanese Institute of Anatolian Archaeology (Çağırkan village, Kaman, Kırşehir, Republic of Turkey), during in situ recovery of fragile or degraded remains coming from the Kaman-Kalehöyük, Yassıhöyük and Büklükale archaeological excavations near Kaman. Slow sublimation noted by the Conservation and the Human Osteology Departments has interfered with the study, treatment, and processing of these materials. The research aim was to determine whether the fume cupboard in the conservation laboratory, with a wind velocity of 80 m/s, could be used to effectively accelerate the sublimation rate of CCD on archaeological objects. The sublimation time and rate of CCD applied to materials of different porosity, such as charcoal, skull fragments and glass, were tested. The sublimation rates were calculated from changes in weight over time, and results were processed by statistical methods. The placement in the fume cupboard of test specimens treated with CCD decreased the sublimation times by almost 50% compared to those tested in a static environment. It was established that facing test samples with a single layer of open mesh textile adhered with CCD, a practice commonly used on site, has a small influence on CCD sublimation rate.

1. INTRODUCTION

1.1 CCD Physical and Chemical Properties and its use in the cultural heritage field

Cyclododecane (CCD) is a cyclic alkane consisting of a ring of twelve carbon atoms, each bonded to two hydrogen atoms (Boschetti and Borgioli 2007).

It has the appearance of a colorless waxy solid and under ambient pressure it has a melting point of 61 ° C. It is characterized by a high vapor pressure that allows it to sublimate completely, making it extremely attractive for applications in conservation field.

CCD has been successfully applied since 1995 in various conservation phases on different types of art and archaeological objects. The main utility of CCD is that it is not necessary to remove it by chemical or physical treatments, potentially compromising the integrity of the treated object, but the product itself sublimates at normal environmental conditions. CCD can be applied by brush or spray, and it can be used pure, as a molten fluid, or as a solution in nonpolar solvents. Depending on the application method used, CCD can perform a superficial coating function, highly hydrophobic and compact, or in depth consolidation. A high water-repellency is obtained using pure molten CCD, which solidifies as a superficial amorphous, glassy and compact mass, avoiding penetration in depth. In the case of deposition from solution, film morphology depends on film formation speed and the boiling point of the solvent used.

Film morphology, therefore, depends on the application method, porosity of the substrate and film formation speed. (Hangleiter 2000; Anselmi *et al*. 2008).

In the conservation field, CCD has been used as a superficial temporary fixative or preservative; literature has reported several uses of CCD as a temporary fixative on wall paintings surfaces, by applying gauzes impregnated with CCD, and as a superficial consolidant of painting layers on easel paintings (Baldi *et al.* 2009; Borgioli, Boschetti and Splendore 2009); as a temporary sealer for cracks and small fissures before grouting of plasters by mortar injections, in order to protect the plaster surface (Baldi *et al*. 2009); as an adhesive, even for wall paintings (*stacco*) (Hangleiter and Saltzmann 2005).

The product has also been used as a temporary water-repellent on paper, textiles and other water-sensitive surfaces, during conservation treatments based on aqueous solutions (Baldi et *al.* 2009; Brückle *et al.* 1999; Muros and Hirx 2004). It has also been widely used as a temporary consolidant for fragile objects (Stein *et al.* 2000), especially for the recovery, handling and storage of friable or degraded archaeological artifacts, when it is necessary to carry them safely, with the intent to treat them with subsequent conservation interventions (Caspi and Kaplan 2001). In addition, CCD applied on textile bandage has been successfully used in archaeological context for creating rigid reinforcements for block-lifting artifacts, as an alternative to traditional plaster bandages (Baldi *et al.* 2009). The use of CCD on archaeological objects is further promoted by the fact that it does not interfere with C14 dating (Pohl *et al*. 2009).

1.2 Sublimation and sublimation rate

Sublimation is a change of a substance from solid phase to vapor phase without the formation of intermediate liquid; it is an endothermic phase transition that occurs at temperatures and pressures lower than the ones characteristic of the triple point in the phase diagram of a substance (David W. Oxtoby, Gillis and Nachtrieb : 154-156). Since the CCD vapor pressure at triple point exceeds 1 atm, the substance sublimates at room temperature spontaneously. From a molecular point of view, sublimation means molecules escape from a solid surface. The translation energy of these molecules depends on temperature. If sublimation takes place in a closed system, the environment will eventually become saturated by vapor; in these equilibrium conditions, the rate of sublimation of solid CCD matches the rate of deposition of its vapor phase and, for a given time, pressure and temperature, the number of molecules that sublimates is equal to the number of molecules that return to the solid state (ibid. 150-154).

Consequentially, in a static environment such as a closed room without airflow, the gaseous sublimated molecules that remain above the solid are able to return to the solid phase, so that sublimation will be rather slow.

Conversely, if sublimated molecules are continuously removed from the surface of the solid (for example by mean of forced ventilation or aspiration), sublimation will proceed very quickly. Since sublimated molecules cannot return to the solid phase, other molecules will continue to leave the surface of the solid.

From these theoretical assumptions, it follows that the CCD sublimation rate depends primarily on temperature and ventilation conditions, on the amount of CCD used on the object, on the surface area exposed to air, on film thickness and on the porosity and geometry of the treated object.

The CCD sublimation rate can be increased by exposing the treated object to ventilation or high temperatures (Hangleiter 2000). Conversely, the sublimation rate may be delayed by:

- protecting the treated object from high temperatures and air currents;
- covering the surface of the treated object with a barrier film as an adhesive, an aluminum or polystyrene foil (Boschetti and Borgioli 2007; Baldi *et al.* 2009);
- storing the treated objects in a sealed container, promoting a vapor saturation condition (Cagna and Riggiardi 2006). According to some sources (Borgioli, Boschetti and Splendore 2009 : 73) the CCD amount necessary to saturate 1 m3 of air is equal to 0.7 ml.

1.3 Research aim

CCD is a material used at the Conservation Department of the JIIA-Japanese Institute of Anatolian Archaeology (Çağırkan village, Kaman, Kırşehir, Republic of Turkey), as a temporary consolidant for the in situ recovery of fragile or degraded remains coming from the Kaman-Kalehöyük, Yassıhöyük, and Büklükale archaeological excavations, in order to lift and carry them safely to the conservation laboratory for further definitive conservation interventions. However, as it is not possible to intervene on archaeological findings until complete sublimation of the CCD, the Conservation and Osteology Departments have noted the inconvenience waiting for complete sublimation of the product. This research therefore aims to find a way to increase the sublimation rate of CCD on artifacts coming from these three sites in Turkey, using equip-

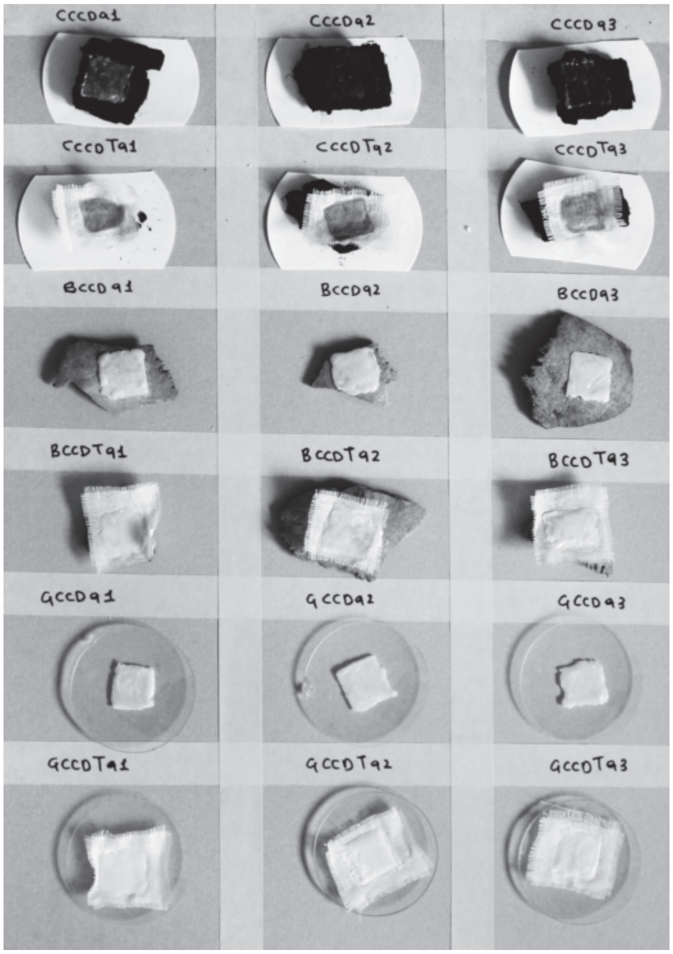


Fig. 1 a-series after CCD application

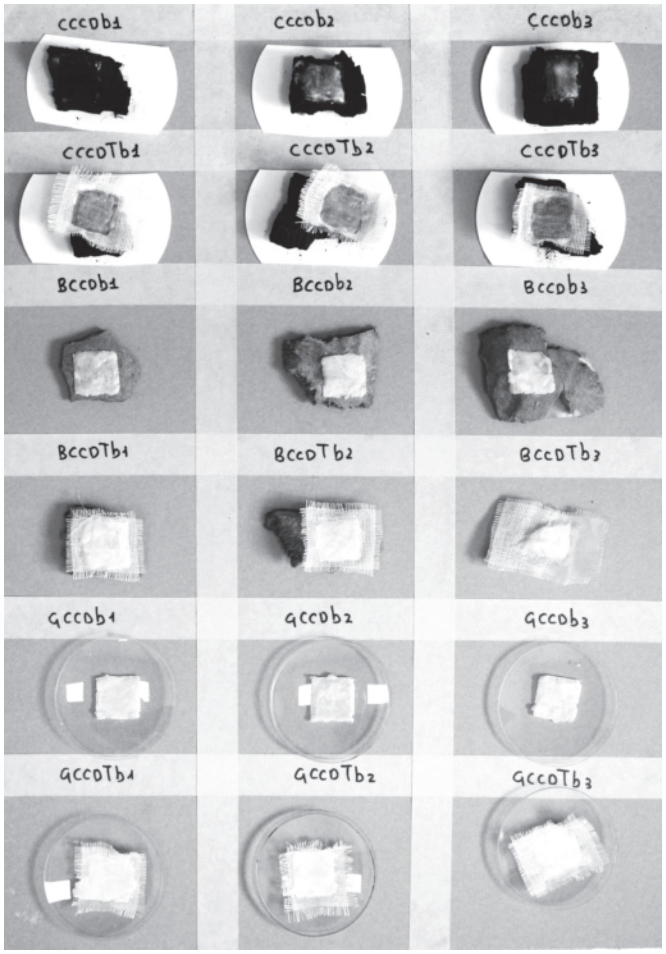


Fig. 2 b-series after CCD application

ment available in the conservation laboratory.

With a recently acquired fume cupboard, the goal of the conservation department was to determine:

- the possibility of accelerating the sublimation rate by placing the treated test pieces in the fume cupboard at controlled air velocity;
- the time required for CCD to sublimate completely from the finds, compared to a static environment;
- whether and to what extent the porosity of the test materials affects the sublimation rate;
- whether and to what extent textile bandages influence the sublimation rate.

2. MATERIALS AND METHODS

It was therefore decided to treat materials of varying porosity, such as charcoal, bone and glass, with CCD. The sublimation rate was determined by measuring changes in weight of samples treated with CCD over time. Samples were weighed every 12 hours. To test whether storage of treated materials in the fume cupboard helps to increase CCD sublimation rate, it was decided to prepare two sets of 18 samples, one of which was stored in a static (closed) environment (a-series) and the other was placed in the fume cupboard (b-series). Each series consisted of 6 charcoal fragments, 6 skull fragments and 6 laboratory watch glasses. The skull fragments from an adult male and the charcoal fragments were recovered during archaeological excavation of the Kaman-Kalehöyük site.

2.1 Samples preparation

After preliminary tests, it was decided to apply 0.70 g of CCD on each test piece (effective average amount applied about 0.69 grams, σ=0.043), distributed over an area of approximately 2.25 cm^2. The CCD was applied to an area delineated by a stencil, 1.5 cm x 1.5 cm, cut from adhesive tape and applied to the surface of the test piece. The stencil was removed once the CCD had solidified. For each type of material (charcoal, bone, glass), half of the samples were covered with textile applied with CDD. The textile chosen to cover the fragments was open mesh cotton, similar to cheesecloth, that is used by the Conservation Department at Kaman-Kalehöyük to face artifacts for lifting in the field.

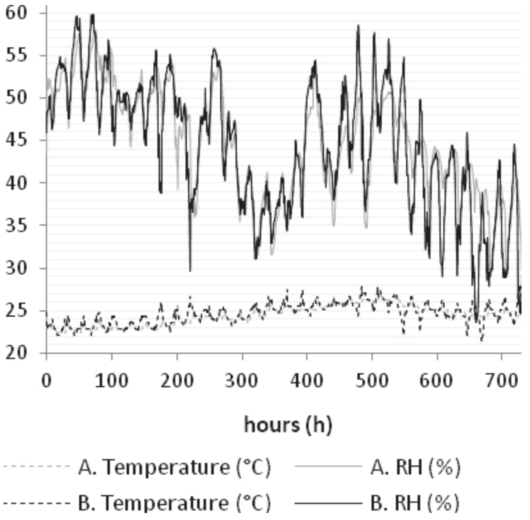
n.	Static Environment	n.	Fume cupboard
1	Ca1	19	Cb1
2	Ca2	20	Cb2
3	Ca3	21	Cb3
4	CTa1	22	CTb1
5	CTa2	23	CTb2
6	CTa3	24	CTb3
7	Ba1	25	Bb1
8	Ba2	26	Bb2
9	Ba3	27	Bb3
10	BTa1	28	BTb1
11	BTa2	29	BTb2
12	BTa3	30	BTb3
13	Ga1	31	Gb1
14	Ga2	32	Gb2
15	Ga3	33	Gb3
16	GTa1	34	GTb1
17	GTa2	35	GTb2
18	GTa3	36	GTb3

Table 1 C=charcoal, B=Bones, T=Textile, G=glass, a=static environment, b= fume cupboard

The CCD (melting point 50-61 °C, Kremer Pigments Inc.) was melted in a water bath, maintaining the water temperature at 60 ° C on a hotplate. It was applied to the samples by dripping from a glass Pasteur pipette that was kept warm before application to prevent solidification of liquid CCD in the pipette. In total 36 test pieces were prepared (*Fig. 1 and Fig. 2*), the nomenclature of which is shown in *Table 1*.

2.2 Test Environments

The a-series was kept in a closed room, at environmental T and RH, while the b-series was placed in a fume cupboard (air velocity equal to 80 m/s, in environmental T and RH. The T and RH were monitored with a data logger in both test areas. Temperature and relative humidity values recorded during the experiment are shown in *Graph 1*. In the static environment the T fluctuated between 22.48 ° C and 27,12 ° C (ΔT_{max} = 4,64 ° C); the maximum RH reached was 58 % and the lowest 29,6 % (ΔRH_{max} = 28,4 %). In the fume cupboard both atmospheric temperature and relative humidity ranges were higher; the T fluctuated between 21,33 ° C and 27,91 ° C (ΔT_{max} = 6,58 ° C); the maximum



Graph 1 Temperature and relative humidity values recorded over 800 hours, starting from 12 July 2011 to 12 August 2011 for test series a and b; a = closed room; b = fume cupboard

RH reached was 59,9 % and the lowest 23,6 % (ΔRH_{max} = 36,3 %).

2.4 Analytical Instruments

The equipment used in the experiment was available in the Conservation Laboratory:

- UWE NJW-600 digital scale (capacity 600 g x 0,02 g);
- Pasolini HP-300 hot plate with temperature control;
- ENILAB fume cupboard (www.enilab.com.tr). Air velocity was measured with a KIMO LV-110 anemometer;
- HOBO data loggers.

3. RESULTS AND DISCUSSION

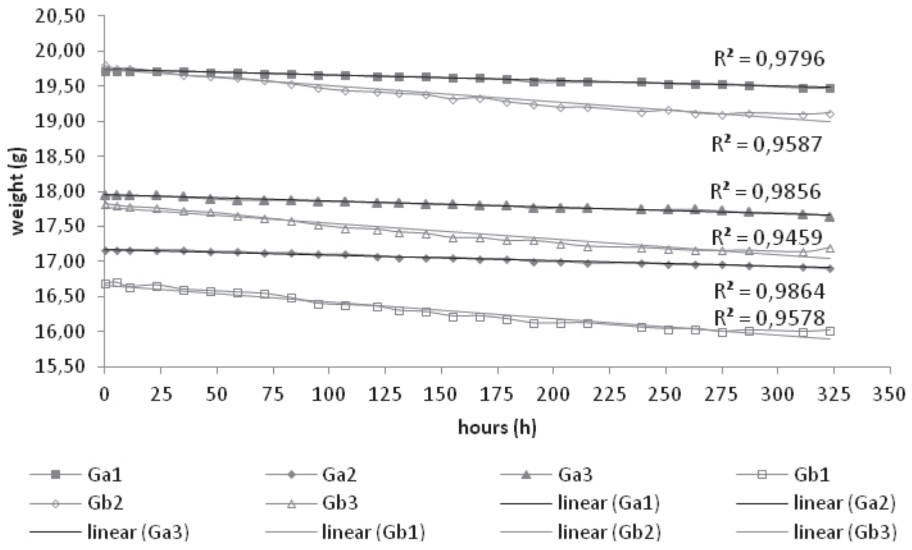
Graphs of test sample weight loss (grams) over time (hours) were prepared (*Graph 2*).

Using ordinary least squares method (OLS), equations of the linear regression models were found in order to approximate experimental data with trend lines, which fit sets of data points.

For each line the value of determination coefficient (R^2) was calculated, which measures how lines fit points trends. All determination coefficients found were such that $0.88 < R^2 < 0.99$, demonstrating that acquired data approximated a linear function. Starting from the slopes of the regression lines, the sublimation rate and time values were obtained. For each typology of test sample, the arithmetic mean of these values was calculated, together with standard deviation (σ) and standard error (ε). Similarly, for each type of test sample, both absolute and percentage variations on mean sublimation time and rate values have been calculated:

- applied to test samples stored in a static environment compared to those in a fume cupboard;
- applied to test samples with textile compared to those without textile;
- applied to materials of different porosity (comparison between glass, bone, and charcoal)

The numerical results obtained are summarized in *Table 2*.



Graph 2 Weight variations over time of glass samples treated with CCD stored in static environment and in fume cupboard. Linear regression models and determination coefficient (R2)

	Vs (g/h)	Ts (h)
Ca1	0,002	450,937
Ca2	0,001	569,321
Ca3	0,001	541,944
μ (Ca)	0,001 ±0,0001 (σ=0,0001)	520,734 ±35,782 (σ=61,977)
Cb1	0,001	506,211
Cb2	0,002	279,487
Cb3	0,002	342,097
μ(Cb)	0,002±0,0003 (σ=0,001)	375,931±67,601 (σ=117,088)
Var.(Cb-Ca)	+0,001	-144,802
Var. (Cb-Ca)%	+ 45,7%	-27,8%
CTa1	0,001	655,057
CTa2	0,001	603,232
CTa3	0,001	572,123
μ (CTa)	0,001±0,00004 (σ=0,0001)	610,137±24,189 (σ=41,896)
Var.(CTa-Ca)	-0,0002	+89,403
Var.(CTa-Ca)%	-15,2%	+17,2%
CTb1	0,002	308,160
CTb2	0,002	279,487
CTb3	0,002	342,097
μ(CTb)	0,002 ±0,0001 (σ=0,0002)	309,914±18,095 (σ=31,342)
Var.(CCCDTa-CCCDTb)	+0,001	-300,223
Var.(CTa-CTb)%	+97,6	-49,2%
Var.(CTb-Cb)	+0,0003	-66,017
Var (CTb-Cb)%	+15,0%	-17,6%
Ba1	0,001	462,781
Ba2	0,001	553,295
Ba3	0,002	447,768
μ (Ba)	0,001±0,0001 (σ=0,0002)	487,948±32,960 (σ=57,088)
Bb1	0,002	304,344
Bb2	0,002	294,787
Bb3	0,002	277,734
μ(Bb)	0,002 ±0,0001 (σ=0,0001)	292,288±7,783 (σ=13,480)
Var. (Bb-Ba)	+0,001	-195,660
Var. (Bb-Ba)%	+65,7%	-40,1%
BTa1	0,001	559,560
BTa2	0,001	504,884
BTa3	0,001	543,231
μ (BTa)	0,001±0,00004 (σ=0,0001)	535,892±16,204 (σ=28,067)
Var. (BTa-Ba)	-0,0001	+47,944
Var. (BTa-Ba)%	-9,6%	+9,8%
BTb1	0,002	305,870
BTb2	0,002	304,802
BTb3	0,002	302,223
μ (BTb)	0,002±0,00001 (σ=0,00001)	304,298 ±1,083 (σ=1,875)
Var. (BTb-BTa)	+0,001	-231,593
Var. (BTb-BTa)%	+75,8%	-43,2%
Var. (BTb-Bb)	0,0001	+12,010
Var. (BTb-Bb)%	-4,1%	+4,1%
Ga1	0,0008	830,9782
Ga2	0,0009	784,9227
Ga3	0,0009	782,2822
μ (Ga)	0,0009±0,00002 (σ=0,00003)	799,394 ±15,810 (σ=27,384)
Gb1	0,002	288,265
Gb2	0,002	300,284
Gb3	0,002	305,551
μ(Gb)	0,002±0,00004 (σ=0,00007)	298,033 ±5,115 (σ=8,860)
Var. (Gb-Ga)	+0,001	-501,361
Var. (Gb-Ga)%	+168,2%	-62,7%
GTa1	0,001	602,730
GTa2	0,001	900,723
GTa3	0,001	777,443
μ(GTa)	0,001±0,0001 (σ=0,0002)	760,299±86,449 (σ=149,735)
Var.(GTa-Ga)	+0,0001	-39,096
Var.(GTa-Ga)%	+8,0%	-4,9%
GTb1	0,002	296,154
GTb2	0,002	342,381
CTb3	0,002	302,852
μ(GTb)	0,002±0,0001 (σ=0,0001)	313,795±11,776 (σ=20,397)
Var. (GTb-GTa)	+0,001	-446,503
Var. (GTb-GTa)%	+136,7%	-58,7%
Var. (GTb-Gb)	0,0001	-15,762
Var. (GTb-Gb)%	-4,7%	+5,3%

Table 2 Vs, CCD sublimation rate; Ts, time required for complete sublimation of CCD applied on samples; h, hours; g, grams; μ(xxx) data arithmetic mean; σ, standard deviation; Var.(xxb-xxa) and Var.(xxb-xxa)%, absolute and percentage variations between sublimation time and rate of CCD comparing test samples from the fume cupboard with those from static environment; Var.(xTx-xx) and Var.(xTx-xx), absolute and percentage variations between sublimation time and rate of CCD comparing test samples with and without textile.

3.1 Results by Category (*Table 1, Table 2*)

CCD applied on charcoal - static environment (Ca1-Ca3)

The CCD sublimated from the charcoal test samples stored in a static environment with a mean time approximately equal to 520 hours (~ 21 days). Compared to the other sample types, charcoal showed a greater oscillation; this is an anticipated result, since the high porosity of the material caused it to be more susceptible to environmental temperature and relative humidity changes.

CCD applied on charcoal - fume cupboard (Cb1-Cb3)

The CCD sublimated from the charcoal test samples subjected to forced aspiration in a mean time approximately equal to 375 hours (~ 16 days); compared to analogous test samples stored in a static environment, mean sublimation time was reduced by almost 30%.

CCD applied with textile on charcoal - static environment

The mean sublimation time of CCD applied with textile on charcoal test samples stored in a static environment was ~ 610 hours (~ 25 days). An increment in mean sublimation time of about 17% was observed compared to analogous test samples treated only with CCD.

CCD applied with textile on charcoal - fume cupboard

The CCD applied with textile on charcoal that was kept in the fume cupboard sublimated in a mean time of ~ 309 hours (~ 13 days); mean sublimation time was reduced by almost 50%, compared to the analogous test samples kept in a static environment.

The CCD sublimated from charcoal covered with textile in slightly less mean time (reduction of about 18%) compared to the charcoal treated with only CCD.

CCD applied on skull fragments - static environment

The CCD sublimated from the skull fragments stored in the static environment in mean time equal to 487 hours (~ 20 days), reduced by almost 6% compared to the mean sublimation time of CCD applied on charcoal test samples stored in the same conditions.

CCD applied on skull fragments - fume cupboard

The CCD sublimated from the skull fragments stored in the fume cupboard in mean time of about 292 hours (~12 days), reduced by almost 40% compared to the mean sublimation time of CCD applied on skull fragments in the a-series. The CCD sublimated from these bone fragments in mean time reduced by almost 22% compared to the charcoal test samples.

CCD applied with textile on skull fragments - static environment

The mean sublimation time of CCD applied on skull fragments with textile was about 535 hours (~ 22 days). The presence of textile had the effect of increasing the mean sublimation time by about 10%. The mean sublimation time of CCD applied on bone fragments was reduced by almost 12% compared to the charcoal test samples stored in the same conditions.

CCD applied with textile on skull fragments - fume cupboard

The mean sublimation time of CCD applied on skull fragments with textile was about 304 hours (~13 days), reduced by almost 43% compared to the analogous test samples stored in a static environment. The presence of textile had the effect of decreasing CCD mean sublimation time by about 4%, compared to the analogous test samples treated only with CCD in the same conditions. Compared to charcoal test samples stored in the same conditions, the CCD mean sublimation time was reduced by almost 2%.

CCD applied on glass - static environment

The CCD applied on glass (*Graph 2*) sublimated in a mean time of about 799 hours (~ 33 days). Compared to the test bones samples, the mean sublimation time increased about 64%.

CCD applied on glass - fume cupboard

CCD applied on glass stored in the fume cupboard (*Graph 2*) sublimated in a mean time of about

298 hours (almost 13 days), about 70% lower than the analogous test samples stored in a static environment. The mean sublimation time of CCD applied on glass was about 2% higher than the skull fragments stored in the same conditions.

CCD applied with textile on glass – static environment

The CCD applied with textile sublimated from the glass samples stored in the static environment in a mean time of about 760 hours (~ 31 days). The mean sublimation time was reduced by about 5% compared to analogous test samples treated with only CCD. The mean sublimation time of CCD applied on glass increased by 42% compared to the analogous bones samples.

CCD applied with textile on glass - fume cupboard

The mean sublimation time of CCD applied on glass with textile stored in the fume cupboard was about 313 hours (~ 14 days); compared to analogous test samples stored in a static environment, the mean sublimation time was reduced by almost 60%. The presence of textile had the effect of increasing the sublimation time by 5% compared to those treated only with CCD.

The CCD sublimation time was longer by about 3% compared to the bone test samples in the same conditions.

3.2 CCD sublimation time related to samples typology

Table 3 shows mean, maximum, and minimum sublimation times of CCD used on the different test sample typologies kept in a static environment.

	Ts (h)	Ts_{max} ; Ts_{min} (h)
GTa	760,299 ±86,449*	(846,748 ; 673,850)
Ga	799,394 ±15,810*	(815,205 ; 783,584)
CTa	610, 137 ±24,189*	(634,326 ; 585,949)
Ca	520,734 ±35,782*	(556,516 ; 484,952)
BTa	535,892 ±16,204*	(552,096 ; 519,687)
Ba	487,948 ±32,960*	(520,908 ; 454,988)

Table 3 **Mean (Ts), maximum (Ts_{max}) and minimum (Ts_{min}) sublimation times of CCD applied on different sample typologies in static environment; h, hours: * standard error (ε)**

The porosity of the materials used in testing may be described from high to low as follows: charcoal > bone > glass.

The shortest mean sublimation times were obtained on bone, while the longest were recorded on glass.

It has been reported that CCD sublimation time increases when the porosity of the treated material increases (Hangleiter 2000), and this assumption has been confirmed by the longer sublimation time found on charcoal compared to that on cranial bone. However, the CCD applied on glass was the last to sublimate. This may be attributed to the watch glasses used, which are concave in shape thereby blocking the backflow of air above the solid surface of the CCD that was applied in the watch glass cavity. The cupped configuration caused a stagnation of sublimated CCD molecules above the solid CCD, slowing its sublimation rate. Both the low porosity and convex shape of the exterior surface of the cranial fragments are the factors that contributed mostly to the highest sublimation rate reached by these test samples.

Table 4 shows mean, maximum, and minimum sublimation times of CCD used on test samples kept in the fume cupboard.

	Ts (h)	Tsmax , Tsmin (h)
Cb	375,913 ±67,601*	(443,532 ; 308,331)
CTb	309,914 ±18,095*	(328,010 ; 291,819)
GTb	313,795 ±11,776*	(325,572 ; 302,019)
BTb	304,298 ±1,083*	(305,381 ; 303,216)
Gb	298,033 ±5,115*	(303,148 ; 292,918)
Bb	292,288 ±7,783*	(300,071 ; 284,506)

Table 4 **Mean (Ts), maximum (Ts_{max}) and minimum (Ts_{min}) sublimation times of CCD applied on different sample typologies in fume cupboard; h, hours; *standard error (ε)**

Table 4 shows that in the fume cupboard tests the minimum sublimation time was obtained on the skull fragments, while the maximum sublimation time was obtained on charcoal. Probably, in this case, the forced aspiration had the effect of removing sublimated molecules above the CCD film, minimizing the problem of vapor stagnation and consequent sublimation rate decrease, caused by the concave shape of the watch glasses. So, in this case, test sample shape and configuration had less effect on the sublimation time whereas porosity was of greater influence.

The greater standard error value on sublimation time and rate mean values of CCD used on the charcoal samples was probably due to the fracturing and subsequent heterogeneity of the charcoal that allowed the CCD to penetrate to different degrees. Therefore sublimation time and rate values may differ substantially from one charcoal test sample to another.

3.3 Effect of forced air velocity on CCD sublimation time

Table 5 shows the percentage decrement of mean sublimation time of CCD applied on test samples in the fume cupboard, compared to those in a static environment.

	ΔTs (h)
C	-27,8% ±19,9%*
B	-49,2% ±6,9%*
G	-40,1% ±8,3%*
CT	-43,2% ±3,2%*
BT	-62,7% ±2,6%*
GT	-58,7% ±12,9%*
μΔTs	-49,0% ±9,4%*

Table 5 CCD mean sublimation time percentage decrement (ΔTs) caused by forced aspiration, for the different typologies of samples; μΔTs, weighted mean; h, hours; *standard error (ε)

On average, the use of the fume cupboard decreased the CCD sublimation time by almost 50% compared to the static environment.

3.4 Effect of textile on CCD sublimation time

Table 6 shows CCD sublimation time percentage variations on test samples treated with textile compared to those treated with only CCD.

	ΔTs (h)
CTa	+17,2 ±11,5%*
BTa	+9,8 ±6,6%*
GTa	-4,9 ±19,2%*
CTb	-17,6 ±22,8%*
BTb	+4,1 ±6,2%*
GTb	+5,3 ±4,2%*
μΔTs	+2,2% ±11,2*%*

Table 6 CCD sublimation time percentage variations (ΔTs) on samples treated with textile compared to those treated with only CCD. μΔTs, weighted mean; h, hours; *standard error (ε)

The presence of textile on test samples, on average, increased the sublimation time by ± 2% compared to analogous test pieces treated only with CCD. However, the standard error value (± 11%) is very elevated compared to the value of the mean (2,2%) and, therefore, the result is not considered very significant. Textile increased the sublimation time for bone in both test conditions whereas it demonstrated opposing results on bone and glass. It can be concluded that the presence of a layer of open mesh cotton textile had little effect on the CCD sublimation time.

4. CONCLUSIONS

4.1 Increasing sublimation rate in the fume cupboard

The fume cupboard was found to be a useful apparatus to accelerate the sublimation rate of CCD applied on archaeological finds coming from Kaman-Kalehöyük site. Samples tested in the fume cupboard required approximately half the time required for complete sublimation of the CCD compared to test samples kept in the static environment. Future studies could be conducted to evaluate the relationship between air velocity and sublimation of CCD to further examine the mechanisms by which air velocity affects CCD sublimation, in order to achieve real control of CCD sublimation time.

The presence of the textile bandage had a minor influence on CCD sublimation times. Evidently a single layer of textile was not sufficient to affect the sublimation time in a substantial way, probably due to the open mesh of the textile chosen, which facilitated access of the air flow to the surface of the test pieces.

It was noted that the skull fragments without textile were the first to sublimate in both the fume cupboard and in the static environment. This is probably due to the low porosity of the exterior surface of the cranial bones, their good state of preservation, as well as their convex shape that facilitated airflow.

The longest sublimation times were recorded for the glass test samples without textile in the static environment (*Graph 2*) and for the charcoal test samples without textile in the fume cupboard. Probably the concave shape of the watch glasses obstructed airflow over the CCD film used in the experiment, causing sublimation times to increase. Porosity, fractures, and heterogeneity account for the slow sublimation of the charcoal.

Charcoal is actually a very porous material that can fracture easily, allowing the consolidant to penetrate deeply thereby delaying CCD sublimation time. Variable penetration of the CCD into the charcoal test samples probably accounted for the great variability of mean sublimation time.

This study leads the way to the creation of the first model to calculate sublimation times of CCD on archaeological objects, when the area of the surface treated and the weight of CCD applied are known. Future studies are called for to discern the relationship between time of sublimation and surface area covered, to correct and validate the first model.

4.2 CCD sublimation rate: an overview

Since the sublimation rate of CCD depends on many experimental variables including temperature, ventilation, film thickness, exposed surface area, porosity of the recipient material, and the configuration of the treated surface, it is not possible to make precise comparisons with other studies. However, similarities may be noted.

Higby found that CCD applied in solution with low boiling point solvents, such as petroleum ether 30 – 40, required much more time to sublimate compared to CCD applied with high boiling solvents, such as rectified petroleum 100 – 140 (Hiby 2008). A similar relationship was found between the boiling point of the solvent and the sublimation rate in a study on Carrara marble and Lecce stone (Anselmi *et al.* 2008). Sublimation was accelerated with n-decane (b.p. 174°C) over cyclohexane (b.p. 86°C) or n-eptane (b.p. 96°C).

The accelerated sublimation achieved in the fume cupboard at Kaman (from about 292 to 375 hours) mirrors the accelerated sublimation obtained with the CCD dissolved in the high boiling point solvent, n-decane (260 hours) (Anselmi *et al.* 2008).

Higby's study (2008) and the current research confirm that the configuration of the surface onto which the CCD is applied has a major impact on the sublimation rate. Higby compared the sublimation rate of drips of dissolved CCD on the concave surface of glass bowls to that of melted CCD on flat glass slides (Higby 2008). He found that CCD dissolved in petroleum ether and rectified petroleum sublimated more slowly from the interior of a glass bowl than did melted CCD from a flat glass slide. In the current study it was found that melted CCD, if applied on a concave shape such as the interior of a watch glass, required more time to sublimate in a static environment, compared to melted CCD applied to flat (charcoal) and convex (cranial fragments) surfaces. A concave configuration holding the CCD may block the backflow of air above the solid surface of the CCD. The cupped configuration causes a stagnation of sublimated CCD molecules above the solid CCD, slowing its sublimation rate.

This research has shown that sublimation of melted CCD may be accelerated in the fume cupboard thereby rendering unnecessary the use of solvents with associated toxicity issues.

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Corinna L. Koch Dandolo
Master of Arts in Conservation-Restoration,
University of Applied Sciences and Arts of
Southern Switzerland (SUPSI).
e-mail: corinnakd@gmail.com