

ODDY TESTS: ADDING THE ANALYTICAL DIMENSION

GAIL GALI BEINER,^{1,2} MIRIAM LAVI,³ HADAS SERI,⁴ ANNA ROSSIN,⁵ OVADIA LEV,⁵
JENNY GUN,⁵ AND RIVKA RABINOVICH^{1,3,6}

¹*National Natural History Collections, The Hebrew University of Jerusalem, Jerusalem 91904, Israel*
gali.beiner@mail.huji.ac.il

²*Palaeontology Lab, Berman Building, Edmond J. Safra Campus, The Hebrew University of Jerusalem,*
Jerusalem 91904, Israel

³*Conservation Laboratory, Institute of Archaeology, The Hebrew University of Jerusalem,*
Jerusalem 91905, Israel

⁴*Conservation Laboratory, The Israel Museum, 11 Rupin Rd., Jerusalem, Israel*

⁵*Laboratory of Environmental Chemistry, The Institute of Chemistry, The Hebrew University of Jerusalem,*
Jerusalem 9171002, Israel

⁶*Institute of Earth Sciences, The Hebrew University of Jerusalem, Jerusalem 91904, Israel*

Abstract.—The so-called “Oddy test” has gained popularity in art and archaeology collections because it is inexpensive to use, and the results are relatively easy to analyze. However, the method is also subjective and does not identify the pollutants. Here we present a modification to the traditional test that addresses these drawbacks and aims at providing solutions. Activated carbon was used to adsorb the volatile emissions generated within the standard Oddy test setup. Gas chromatography–mass spectrometry (GC-MS) analysis of the volatile organic compounds (VOCs) desorbed from the activated carbon detected pollutants within a considerably shorter time frame than the traditional Oddy test and provided both qualitative and quantitative data. GC-MS analysis of volatiles off-gassed during the Oddy test provided information about the VOCs from local brands of materials commonly used for conservation and storage of objects in collections. The use of GC-MS analysis of volatiles improves the Oddy test in a fast, sensitive, and quantitative manner.

Key words.—Oddy test, materials testing, VOCs, GC-MS, Activated carbon.

MATERIALS TESTING IN CONSERVATION—A SHORT REVIEW

The Oddy test is used by museum conservators to gain insight into potential risks of materials used in museum specimen conservation and display due to the emission of volatile organic compounds (VOCs). The Oddy test is inexpensive, is user-friendly, and does not require specialist knowledge to evaluate test results. Over the decades, the original Oddy test system has been modified several times to increase its usefulness and reliability. The classical Oddy test, also known as the “standard accelerated corrosion test” (Thickett and Lee 2004), was originally proposed by A. Werner and developed by W.A. Oddy (Oddy 1973, Banik 2013). Current test protocols tend to be based on later modifications by Green and Thickett (1995), who facilitated the corrosion of copper (Cu), lead (Pb), and silver (Ag) metal coupons by placing all of them together in one vessel with a select amount of a potentially harmful material in the sealed vessel at 60°C and elevated humidity levels for 4 weeks. Others addressed problems with sealing the test vessel to prevent air exchange during testing (Bamberger et al. 1999, Robinet and Thickett 2003). Chen et al. (2007) and Wang et al. (2011) attempted to decrease testing time by substituting the traditional coupons with metal films. Wang et al. (2011) also proposed a unified visual digital analysis system in order to solve the problem of subjective visual analysis. To increase test sensitivity, some used alternative materials to the Cu, Pb, and Ag metal coupons (Collings and Young 1976, Hawkins et al. 1998, Chen et al. 2007, Wang et al. 2011). For example, current protocols for the photographic activity test (PAT) as performed by the Image Permanence Institute (2015) may be described as a development of the setup published by Collings and Young (1976).

Instead of metal coupons, a PAT includes the use of sandwiched layers of detector films with filter paper and tested materials, which were subjected to 70°C and 86% relative humidity (RH) for 15 days to accelerate aging. As with the Oddy test, PAT evaluation involves assessment of changes in comparison with control samples, with final results given in the form of pass/fail.

However, most current museum testing is carried out using variations of the Green and Thickett (1995) design, with metal coupons being subjected to accelerated aging in a closed vessel. The British Museum offers examples of testing results for various materials in their Oddy test database (Thickett and Lee 2004). Analysis of the Oddy tests by museum conservators is still largely visual and depends on the subjective scoring of visual corrosion on the metal coupons in comparison to control coupons. Changes in metal coupons may be attributed to a variety of chemicals such as organic acids (particularly acetic and formic acid), formaldehyde, sulfurous compounds, and carbonyl and nitrogen compounds (Thickett and Lee 2004, Wang et al. 2011). The Oddy test and its variants are unable to identify the contributing pollutants and give no clear indication of the degree of damage to the metal coupons due to volatile organic compounds. This is problematic because the fundamental assumption of the Oddy test is that reactions in metals indicate reactions in nonmetals as well. However, organic compounds, such as acetone or ethanol, which do not affect the tested metals may be detrimental to other object materials but are not detected in a standard Oddy test (Hatchfield 2002).

EVALUATING POTENTIAL RISK TO ORGANIC OBJECTS

Materials that pass the Oddy test are believed to emit only very low levels of acetic acid, formic acid, or formaldehyde, since these substances affect lead (Strlič et al. 2010). However, Strlič et al. (2010) admit that visible changes from these substances are likely to occur long after actual chemical deterioration starts, and organic materials may respond to a different range of pollutants than the three metal coupons in the classical Oddy test. Curran et al. (2014) noted that degradation reactions often begin prior to any visually evident damage on an organic substance. Daniels and Ward (1982), Odegaard et al. (2000), and Thickett and Lee (2004) proposed the use of a series of microchemical spot tests as an alternative to the Oddy test to identify pollutants in cases where time restrictions apply. Spot testing basically pinpoints predefined substances and, thus, poses complications when it is not known what pollutants to expect.

Later research projects focused on finding a suitable adsorbent for VOCs, which may provide a better ability to identify the potential risks to organic materials. For example, several researchers subjected papers made of pure cellulose to aging conditions to examine adsorbence by an organic substrate and provide a standard reference of organic materials (5 days at 100°C [Strlič et al. 2010]; 14 days at 80°C [Curran et al. 2014]). Other examples demonstrate the use of solid sorbents to trap VOCs. Three main types of solid sorbents used include silica gels (molecular sieves), porous organic polymers, and carbon-based porous materials. Each type of sorbent has different characteristics and may trap different VOCs (Salthammer and Uhde 2009). Wu et al. (2006) suggested the use of mesoporous silica as a collector of VOCs. Tenax TA and other commercial sorbents have also been reviewed for their proposed ability to collect VOCs (Harper 2000, Rushworth et al. 2014). Idris et al. (2010) proposed the use of Tenax TA as a VOC collector because it is less susceptible to changes in the RH compared with mesoporous silica.

ACTIVATED CARBON AS AN ADSORBENT FOR MATERIALS TESTING

Activated carbon is charcoal in which the microporosity has been enhanced by activation, usually by steam oxidation (Harper 2000). The heat in this process expands the porosity and increases the specific surface area (Son et al. 2011). Activated carbon is one of the most common sorbents in commercial use (Harper 2000), since it adsorbs most nonpolar and slightly polar VOCs. Because of its high adsorption capability, activated carbon is used to collect NO₂ and other VOCs in low-concentration open space pollution environments (Son et al. 2011). In order to develop a system to easily detect VOCs in an Oddy test setup by museum professionals worldwide, we chose to test activated carbon, since it is widely available and capable of adsorbing a relatively wide range of VOCs. Activated carbon provides an additional dimension to materials evaluation and allows for both the identification and quantification of adsorbed VOCs via passive adsorption. Our study demonstrates how activated carbon can easily be incorporated into the typical Oddy test process. We identified VOCs via thermal desorption (TD), using triple quadrupole (QQQ) GC-MS coupled with a supersonic molecular beam (SMB) electron ion (EI) source (TD-GC-SMB-EI-QQQ-MS; Appendix A). Our goal was twofold: (1) to determine whether activated carbon would successfully detect a range of VOCs within an Oddy test setup and (2) to determine whether we could decrease the needed testing time.

It has been stated that under high relative humidity, such as the Oddy test microenvironment, water can displace adsorbed organic molecules on activated carbon, react with them, or form an immiscible phase on desorption (Harper 2000). This seems to indicate that molecules with low polarity may be difficult to identify and quantify with activated carbon. Nonetheless, the experiments described here present relatively high emissions successfully and consistently repeated in triplicate tests. We found that the experiments detailed below gave us informative readings even of molecules with low polarity, such as toluene, benzene, benzaldehyde, and so on. Previous publications also refer to issues such as competitive adsorption of different VOCs by various adsorbents (e.g., Tétreault 2003). For our purposes here, we aimed to identify and quantify a range of VOCs to provide insight into possible causes of change in materials. Further research is necessary to understand the effect of competitive adsorption, i.e., to understand the interaction of different VOCs emitted by one material and how this affects the identity and quantities of VOCs at each stage of the aging process. Nonetheless, this method may provide useful qualitative and quantitative information for any materials tested within an accelerated aging setup. The proposed setup of accelerated aging tests of emitted VOCs can be used both as a screening test for storage materials and as an analytical tool when the specific goal pollutant is defined for measurement.

EXPERIMENTAL SETUP

We carried out four experiments using the traditional Oddy test setup with three metal coupons (Appendix B) hanging from a nylon monofilament thread inside a 250 ml Erlenmeyer glass vessel, closed with a ground glass stopper and a Teflon ribbon gasket (Fig. 1). The metal coupons were prepared as detailed in Appendix C. Each test was subjected to accelerated aging in a Climacell[®] incubator set to 60°C for 28 days. Our aim was to create a simple setup for identifying and quantifying VOCs with potential effects on organic, as well as inorganic, materials. To this end we added a VOC collector to the usual Oddy test setup. Our selected VOC collector was activated carbon.

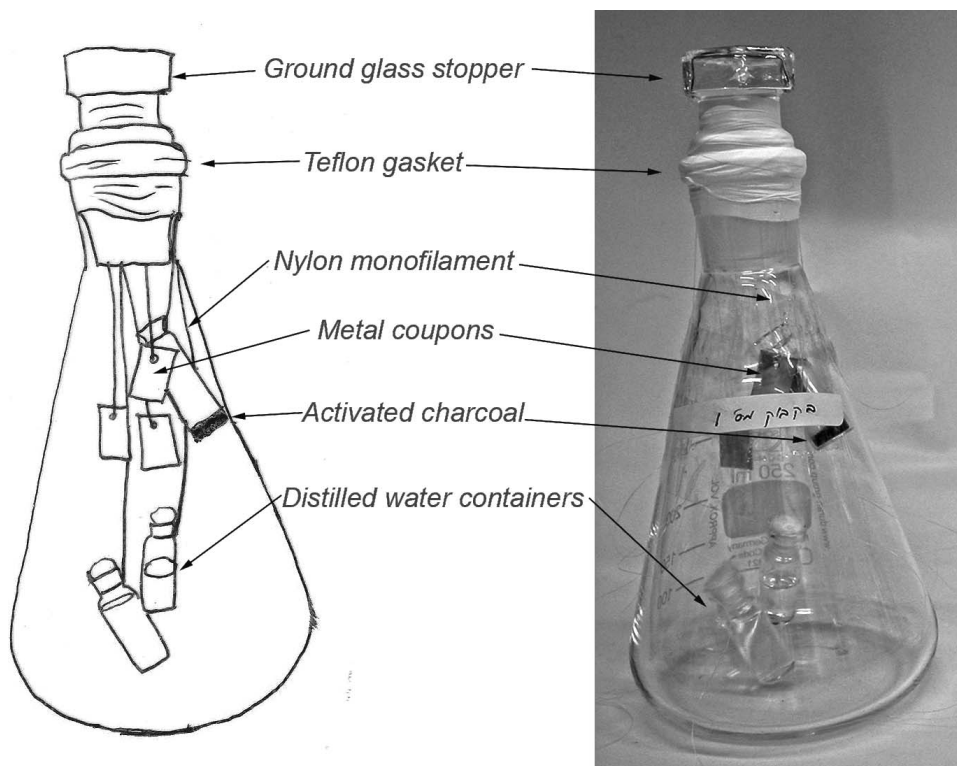


Figure 1. Modified Oddy test setup with activated carbon.

TEST I—EFFECT OF ACTIVATED CARBON ON THE ODDY TEST

We tested whether activated carbon had any independent effect on the metal coupons used within the Oddy test setup. Small glass vessels containing 3 ml distilled water were suspended with nylon monofilament threads inside two Erlenmeyer vessels (250 ml each), rinsed with H_2SO_4 and distilled water. Each container contained a lead, copper, and silver coupon and were subjected to 60°C for 28 days. One of the containers also contained a small glass vessel with activated carbon powder (specifications described in Appendix D).

TEST II—MATERIAL CORROSION

To exclude activated carbon as a source of VOCs, we examined whether glassware cleaning protocol or the distilled water source could have been the cause of the results obtained from Test I. Six Erlenmeyer vessels (250 ml each) were prepared with metal coupons (Cu, Ag, Pb) (Appendix C) and 3 ml triple distilled water. Four of these vessels contained activated charcoal. Three Erlenmeyer flasks were cleaned with H_2SO_4 , and three were cleaned with Alconox[®] (Appendix B), which is a widely used laboratory detergent for glassware.

TEST III—ODDY TEST COMBINED WITH GC-MS ANALYSIS

The seven materials tested in this experiment (Table 1) were of the type generally used for storage and, therefore, often are in direct contact with objects in the collections and/or

Table 1. Test III: Materials tested.

Material name	Material composition	Supplying company
Kalkar	Polystyrene blocks	Ein Acarmel
Palfoam®	Cross-linked polyethylene foam	Palziv
Polygal®	Polypropylene board	Polygal Plastic Industries Ltd.
Jiffy foam/Ethafoam® equivalent	Polyethylene foam	D.C. Pack Ltd.
Lock&Lock® box	Polypropylene, polyethylene, and silicone	S.D Import &Marketing Household & Gift Ltd.
Biresin S12®	Liquid aromatic epoxy resin for casting	Cermat Ltd.
Free Form Air®	Aromatic epoxy dough	Cermat Ltd.

are enclosed with objects for long periods of time. All the materials were sourced from local suppliers to test locally available products, since materials testing for conservation has not been published in Israel. Thus, local conservators often hesitate to use locally available products and feel obliged to import expensive supplies from overseas. Excavators and researchers often use locally available materials due to cost restrictions, but these materials have never been tested for use with our finds and collections.

In this experiment, we tested the effect of seven materials (Table 1) and distilled water on Cu, Ag, Pb coupons prepared according to Appendix C. The experiment was replicated three times and also included a triplicate control, where vessels contained no materials other than activated carbon and 6 ml triple distilled water. Materials requiring preparation (e.g., epoxies) were mixed and set about a year prior to the experiment. Visual analysis of the metal coupons following the experiment period was encoded in a simple three-color code, as shown in Table 2. The color red denotes extreme changes in the metal coupon, as compared with untested coupons of the same metal. Yellow indicates little change, while green indicates no change at all.

TEST IV—DOES GC-MS SHORTEN ODDY TESTING?

GC-MS analysis is a relatively sensitive tool that is capable of identifying pollutants in very small quantities. Therefore, it was postulated that much shorter time periods were required than the usual 28 days allocated to the traditional Oddy test. We used GC-MS analysis to determine whether the time needed for materials testing could be shortened compared with the Oddy test alone.

Eighteen Erlenmeyer vessels (250 ml) were divided into three groups. Each group remained in the Climacell® incubator for a different length of time: 2 days, 1 week, and 2 weeks. Each group consisted of six vessels: two controls, two with 0.50 g “jiffy foam” and two with 10 g Free Form Air® epoxy. These materials were chosen because they had shown significant visual change in the coupons in the main experiment. One vessel of each type (control, jiffy foam, and epoxy) contained analytical metal coupons (Cu, Ag, Pb), prepared as described in Appendix C. All of the vessels contained activated carbon and 6 ml laboratory-grade distilled water.

RESULTS

In Test I, the lead (Pb) coupons in the vessel with the activated carbon exhibited white spots after 28 days in the incubator (Fig. 2a). Copper (Cu) and silver (Ag) coupons in the two vessels exhibited the same appearance. We used a high-resolution scanning electron microscope (SEM) to examine the white spots for VOC-related products; accelerating

Table 2. Test III: Green = hardly any change compared with untested coupons; Visual analysis of metal coupons. Yellow = some change observed; Red = extreme change observed.

	Tested material	Grams	Copper	Silver	Lead
1	Blank A	n/a	Yellow	Green	Green
2	Blank B	n/a	Yellow	Green	Green
3	Blank C	n/a	Yellow	Green	Green
4	Kalkar®	1.08	Yellow	Green	Green
5	Kalkar®	1.02	Yellow	Yellow	Green
6	Kalkar®	1.06	Yellow	Green	Green
7	Palfoam®	2.02	Yellow	Green	Green
8	Palfoam®	2.03	Yellow	Green	Green
9	Palfoam®	2.06	Yellow	Green	Green
10	Polygal®	2.06	Yellow	Green	Red
11	Polygal®	2.02	Red	Yellow	Yellow
12	Polygal®	2.02	Yellow	Green	Yellow
13	Jiffy foam	0.48	Yellow	Green	Red
14	Jiffy foam	0.49	Yellow	Yellow	Red
15	Jiffy foam	0.49	Yellow	Green	Red
16	Lock&Lock	10.16	Yellow	Green	Yellow
17	Lock&Lock	10.04	Green	Green	Red
18	Lock&Lock	10.05	Yellow	Green	Red
19	Biresin S12	10.03	Red	Yellow	Yellow
20	Biresin S12	9.95	Red	Yellow	Yellow
21	Biresin S12	10.12	Red	Yellow	Yellow
22	Free Form Air®	9.9	Red	Yellow	Yellow
23	Free Form Air®	10.04	Red	Yellow	Yellow
24	Free Form Air®	10.07	Red	Yellow	Yellow

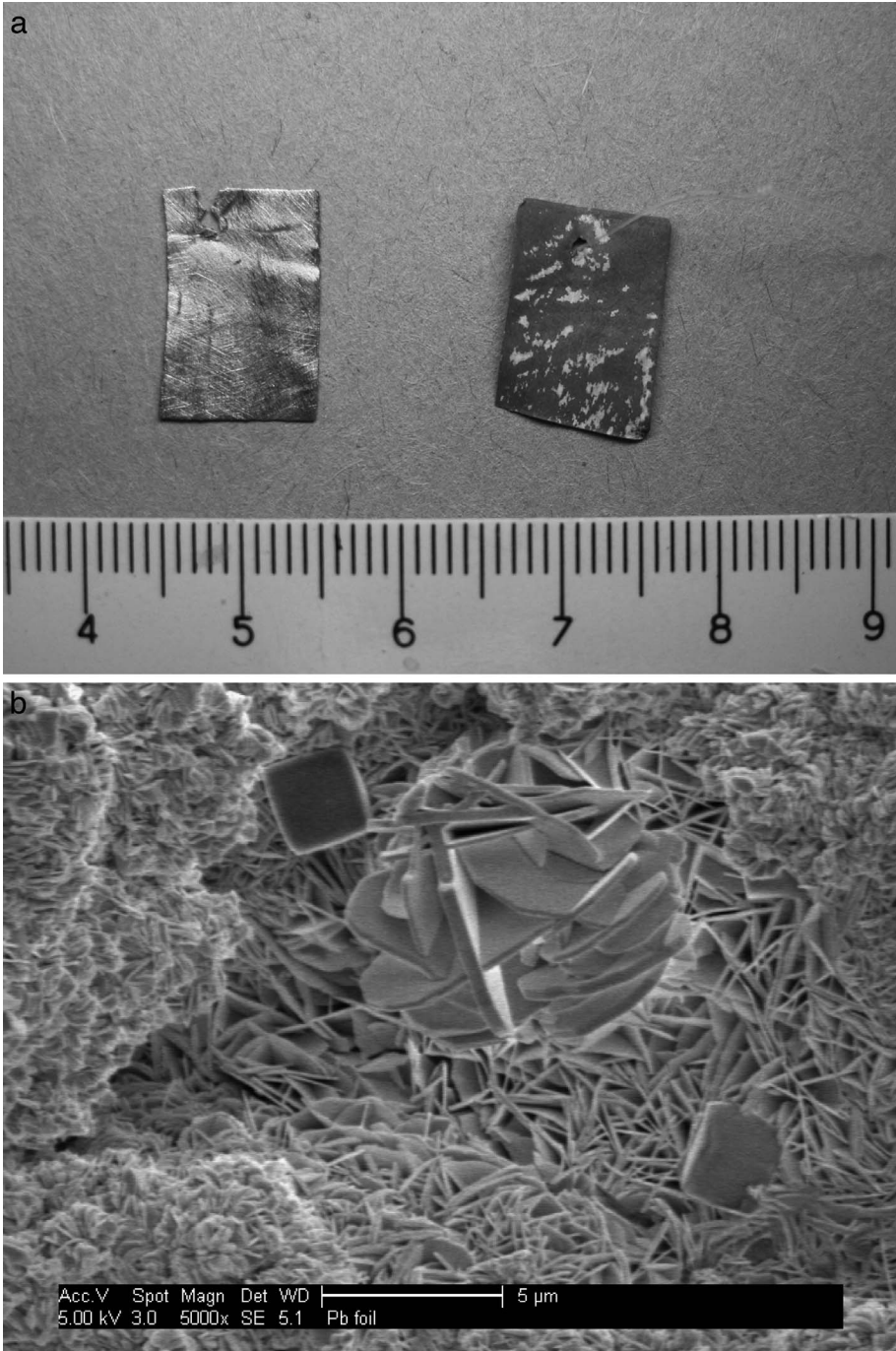


Figure 2. Test I: Corrosion on lead coupon (a) photographic image; (b) SEM imaging.

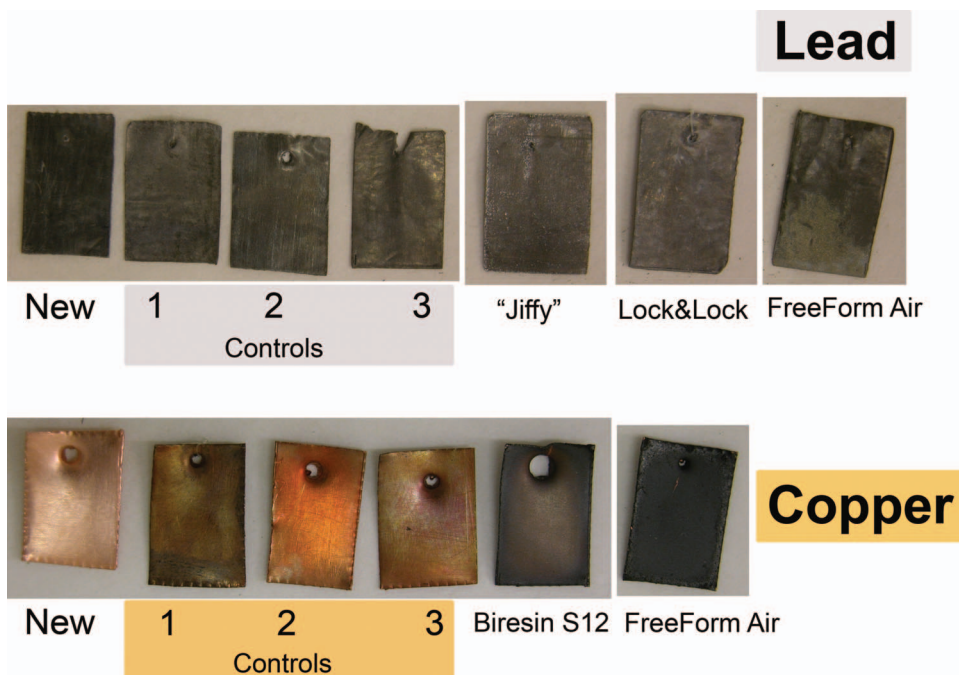


Figure 3. Test III: Visual comparison of coupons.

voltage was set at 5–15 kV with 5 mm working distance; imaging was conducted using high-resolution mode with a through-the-lens detector. SEM imaging for the “spotty” lead coupons (Fig. 2b) gave a clear image of crystals on the surface. However, these crystals contained only the basic corrosion products for lead: lead, oxygen, and carbon. No products that could be directly attributed to the presence of activated carbon were found. In Test II, Accelerated aging produced no unusual appearance of the metal coupons. Because vessels contained either activated carbon or not, we concluded that the carbon had not caused the white spots in Test I. Half of the Erlenmeyer vessels were cleaned with one cleaning protocol and half with a different cleaning protocol, so the cleaning agents had not caused the white spots. However, the distilled water in Test I had been purchased from a store, while the distilled water used in Test II was laboratory grade, highly processed triple distilled water with less than 100 ppb total organic carbon concentration. Therefore, it is likely that the white spots from Test I had been caused by pollutants in insufficiently pure distilled water. Tests I and II therefore determined that activated carbon does not independently affect analytical metal coupons and that the quality of the distilled water is of particular importance.

In Test III, both type of epoxies (Biresin S12[®] and Free Form Air[®]) caused extreme changes in Cu coupons, though the color change was significantly more pronounced in the Free Form Air[®] coupons (Table 2). The thin polyethylene foam (jiffy foam) and Lock&Lock[®] box caused extreme changes in the appearance of the Pb coupons. The Polygal[®] gave an uneven result. Some change was observed in all Cu coupons in all test vessels, including controls. Ag and Pb coupons were moderately affected in all epoxy-containing vessels. The visible changes to Cu and Pb coupons can be seen in Figure 3. Results for GC-MS analysis of activated carbon from the main experiment are shown in Table 3. X-ray fluorescence (XRF) analysis of all the metal coupons, including controls,

Table 3. Test III: Qualitative and quantitative GC-MS results.

Tested	Analysis	Chemical formula	µg per 1 g sample
Kalkar	Pentane	C ₅ H ₁₂	0.001
	Ethylbenzene	C ₈ H ₁₀	0.01
	Styrene	C ₈ H ₈	1000
Palfoam®	Benzaldehyde	C ₇ H ₆ O	0.01
	Methenamine	C ₆ H ₁₂ N ₄	0.01
	Hydroxy-acetonitrile	C ₂ H ₃ NO	0.01
Polygal®	Unidentified (116 m/z)		0.01
	Ethyl acetate	C ₄ H ₈ O ₂	0.001
Jiffy foam	Unidentified (156 m/z)		0.01
	Tetrachloroethylene	C ₂ Cl ₄	0.01
Lock&Lock®	Methoxy-phenyl oxime	C ₈ H ₉ NO ₂	0.001
	Unidentified (209 m/z)		0.001
Biresin S12®	1,2 benzisothiazole	C ₇ H ₅ NS	0.001
	Benzaldehyde	C ₇ H ₆ O	0.001
	Benzyl alcohol	C ₇ H ₈ O	0.001
Free Form Air®	Benzyl alcohol	C ₇ H ₈ O	100
	Benzaldehyde	C ₇ H ₆ O	1
	Benzonitrile	C ₇ H ₅ N	0.001
	Trimethyl (3-methylphenoxy) silane	C ₁₀ H ₁₆ OSi	0.01
	Benzyl acetate	C ₉ H ₁₀ O ₂	0.1
	Benzamide	C ₇ H ₇ NO	0.01
	5-Methyl 2-phenyloxazole	C ₁₀ H ₉ NO	0.01
	Toluene	C ₇ H ₈	100
	Benzoic acid	C ₇ H ₆ O ₂	1
	Unidentified (221 m/z)		0.001

was performed but did not yield any particular relationship between the tested materials and visual changes in the metal coupons. Test III emphasized that some visual change is liable to occur due to accelerated aging alone, regardless of whether VOC-emitting materials are present or not, since all coupons showed some sort of change after accelerated aging. The comparison with the controls enabled pinpointing visual changes due to tested materials, e.g., from both types of epoxy products to Cu coupons, as well as the less drastic visual changes caused by the local jiffy foam product and the Lock&Lock® box to Pb coupons. The controls also made it possible to identify VOCs attributed to the tested materials. VOCs found in controls were not included in Table 3. In addition, Table 3 only lists VOCs that had appeared in all triplicate tests performed for each material. GC-MS analysis of the activated carbon gave both identification and quantification of VOCs for all of the tested products. The quantification in Table 3 is given in micrograms (µg) per gram (g) of sample. Thus, the total quantity of VOC per any quantity of sample may be easily inferred. Combined with visual analysis, the museum conservator is thus given a particular insight into which VOCs may pose a potential risk. For example, ethylbenzene may not pose a risk at 0.01 µg per 1 g material (Table 3) because the Kalkar® product did not exhibit alarming visual change. The low quantities shown in Table 3 tell us that very small amounts of VOCs may already pose a palpable risk, e.g., 0.01 µg/g tetrachloroethylene in the local jiffy foam product, or 0.001 µg/g for each of the two substances identified for the Lock&Lock® box.

In Test IV, visual analysis of the metal coupons following accelerated aging (Fig. 4) demonstrated that in the case of the epoxy material, Cu coupons started changing very quickly, within 2 days. Ag and Pb coupons did not appear to be affected even after 1 or

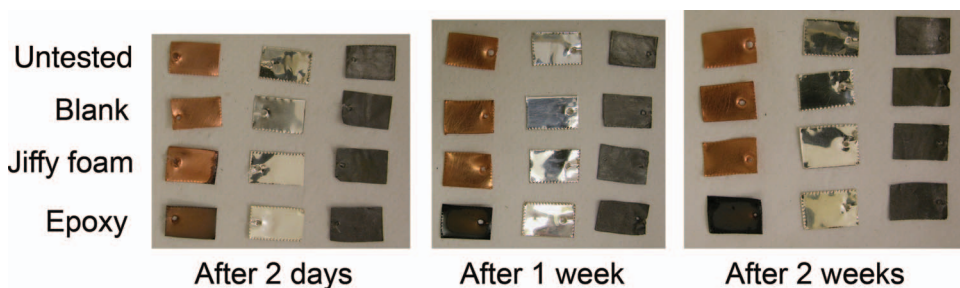


Figure 4. Test IV: Visual comparison of coupons.

2 weeks. The GC-MS analysis of the activated carbon (Table 4) showed that quantities of pollutant per gram of sample rose as time increases from 2 days to 1 week. However, after 2 weeks, concentrations in the epoxy-containing vessels tended to be close to, or even lower than, concentrations after 1 week. Two of the detected ions, the last two shown for the epoxy resin in Table 4, only appeared in the GC-MS analysis after 1 week in the aging chamber, indicating that at least 1 week is required for effective VOC collection and analysis. Test IV answered the interesting question regarding the minimum duration required for a useful standard Oddy test, i.e., 1 week. In fact, shorter testing time may reflect VOC off-gassing more accurately, because some VOCs undergo further reactions over time. Longer testing timeframes may therefore result in some VOCs not being noticed or identification of products of secondary reactions. For example, the only VOC found in Test III but not in Test IV for Free Form Air® epoxy was benzonitrile. This may be because it is formed over time as a secondary product of a VOC reaction rather than as a direct pollution emitted by the tested material.

CONCLUSIONS

Our results show that activated carbon may be used successfully to determine the presence of VOCs within an Oddy test setup. Activated carbon may even enable quantification of these VOCs, although no single adsorbent is capable of retaining all VOCs. Salthammer and Uhde (2009) indicated that either a combination of adsorbents or a very specific choice for the actual analytical problem is necessary. McGath et al. (2014) compared different adsorbents (silica gel powder, zeolite, and activated carbon), with the conclusion that each adsorbent shows a different range of adsorption. Here, activated carbon was chosen due to availability, ease of use, and basic ability to absorb a relevant range of VOCs. Furthermore, the average museum conservator can use activated carbon within the framework of a regular Oddy test, which enables useful testing of local products from small suppliers. Experiment replication, comparison with control conditions, and a focus only on high peaks in the GC-MS analysis evident in all three repetitions of each test made it possible to obtain meaningful results even in high RH conditions.

“Cross infection” or cross-effects of different pollutants in a given environment was not tested here but remains a concern (Tétreault 2003, and Curran et al. 2014), i.e., cross infection may involve VOCs emitted from multiple materials in one environment. Our experiments tested only one material in each vessel and therefore did not deal directly with this subject, but there still remains the question of competition between different VOCs from a single material. McGath et al. (2014) demonstrated how different adsorbents exhibited different “adsorption timelines,” broadly beginning with a linear increase in adsorption, continuing to a failure in linearity, and finally a decrease in

Table 4. Test IV: VOC detection in relation to test duration.

Material	Compound name	Chemical formula	Concentration in µg/g (standard deviation)		
			3 days	1 week	2 weeks
Jiffy foam	Tetrachloroethylene	C ₂ Cl ₄	0.002 (0.004)	0.0052 (0.0012)	0.0134 (0.0019)
	Unidentified (156 m/z)		N.D.	0.001	0.0007
Free Form Air®	Toluene	C ₇ H ₈	2.8 (0.4)	5.7 (0.8)	5.9 (0.1)
	Benzyl alcohol	C ₁₄ H ₁₄ O ₂	1.8 (0.1)	20 (0)	18 (0.8)
	Benzyl acetate	C ₉ H ₁₀ O ₂	0.0215 (0.0159)	0.0352 (0.0106)	0.0368 (0.0235)
	Unknown (221 m/z)		0.0549 (0.0445)	0.0239 (0.0109)	0.0084 (0.0032)
	Benzaldehyde	C ₇ H ₆ O	2.4 (0.3)	3.2 (0.4)	2.9 (0.1)
	Trimethyl (3-methylphenoxy) silane	C ₁₀ H ₁₆ O _{Si}	0.0316 (0.0026)	0.0226 (0.0059)	0.0076 (0.0021)
	Unknown (194 m/z)		0.1469 (0.0818)	0.0031 (0.0004)	0.0015 (0.0008)
	(E)-N-Benzyl-1-phenylmethanimine	C ₁₄ H ₁₃ N	0.0008 (0.003)	0.0002 (0)	0.0001 (0)
	Trimethylsilanol	C ₃ H ₁₀ O _{Si}	0.1093 (0.0163)	0.0343 (0.0139)	0.0217 (0.0116)
	Tetramethylsilane	C ₄ H ₁₂ Si	0.054 (0.0706)	0.1184 (0.0036)	0.0295 (0.0054)
	Benzoic acid	C ₇ H ₆ O ₂	0.0369 (0.0124)	0.0508 (0.0134)	0.0716 (0.0034)
	Octamethyl-cyclotetrasiloxane	C ₈ H ₂₄ O ₄ Si ₄	1.4 (0.4)	3 (0.8)	0.7 (0.2)
	5-Methyl-2-phenyloxazole	C ₁₀ H ₉ NO	N.D.	0.0027 (0.0004)	0.004 (0.0001)
	Benzamide	C ₇ H ₇ NO	N.D.	(0)	0.0036 (0)

adsorption. The variation in adsorption timelines could be attributed either to competitive adsorption or to adsorbent saturation. Competitive adsorption may be possible to analyze with the presented setup with activated carbon. Setting up a large database of GC-MS results for Oddy tests of different materials may help give an idea of the actual minimum level of a given VOC needed to cause change in metal coupons or selected organic materials.

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APPENDIX A: GC-MS ANALYSIS

TD-GC-SMB-EI-QQQ-MS analysis was conducted using model 5975 SMB ion source and interface, which were installed on an Agilent GC-QQQ-MS system equipped with 7890A GC and with a 7000A triple quadrupole mass spectrometer (QQQ-MS). A ChromatoProbe direct sample introduction device was mounted on a multimode inlet (MMI). Ten milligrams of charcoal was placed in small ChromatoProbe vials, which were placed into the tube of a ChromatoProbe inlet. The ChromatoProbe allows thermal evaporation of the adsorbed pollutants and their direct introduction into the gas chromatographic capillary without solvent extraction.

The experimental details of the GC-SMB-QQQ-MS analysis and ChromatoProbe have both been described in detail previously (Amirav et al., 2001, 2008; Anna et al. 2011). The injection was done in a splitless mode, with an initial temperature of 65°C for 0.4 minutes, and then ramped at 600°C/min to 300°C. For separation, we used a 30 m long 0.25 mm internal diameter capillary column with 0.25 µm film, Rxi-5ms film (Restek). The helium was used as the carrier gas. The column flow rate was kept at 1 ml/min for 16 minutes, and then ramped at 4 to 3 ml/min. The GC oven temperature was kept at 50°C for 2.5 minutes, followed by a ramp at 10°C/min to 310°C, and a final hold time of 10 minutes. The quadrupole mass spectrometer was operated in a total ion chromatogram (TIC) full scan mode at a scan rate of 3.4 cycles/sec (297 ms/cycle) over a scan range of 42–500 AMU.

Identification of molecules was performed using a National Institute for Standards and Technology (NIST) library and supported by the Tal-Aviv IAA software kit (Anna et al. 2011; Alon et al., 2006), which takes into account the unique isotopic pattern of different atoms in the analyte and automatically inverts the experimentally obtained isotope abundances into elemental formula information, thus confirming or rejecting the library identification. The technique provides a powerful confirmation tool when heteroatoms with a unique isotopic pattern are present in the impurity.

Only structures that were sensible and both fit in with the NIST library with more than 51% and had a match score of over 900 (out of 1000), plus their isotopic pattern fitted the calculated pattern as determined by the Tal-Aviv IAA software with a matching factor greater than 850 (out of possible 1000), were taken into account.

VOC quantification involved analysis of the known amount of sample during the test procedure and conducting an adsorption with a constant known amount of activated carbon. The intensity of chromatographic peaks normalized by internal standard were recalculated to the concentrations using calibration curves of benzaldehyde and benzoic acid. The uniformity of SMB EI MS was a considerable advantage in this procedure of semiquantification of the VOCs from the materials.

APPENDIX B: SUPPLIERS

Tested Materials

1. Free Form Air® epoxy dough, Smooth-On Inc., 2000 St. John Street, Easton, Pennsylvania 18042, USA, supplied by Ceramat Ltd., Israel.

2. Biresin S12[®], supplied by Cermat Ltd., Israel.
3. Kalkar foam beads, Ein Acarmel, D.N. Hof Acarmel, Israel.
4. Polygal[®] polypropylene structured sheet, supplied by Polygal Plastic Industries Ltd., Ramat HaShofet 19238, Israel.
5. Palfoam[®] (known in Israel as “Palziv”) cross-linked polyethylene foam, supplied by Palziv, Ein Hanatziv D.N. Bet Shean 10805 Israel.
6. Closed cell polyethylene foam in rolls, 2 mm thick (the Israeli equivalent of Jiffy foam), supplied by D.C. Pack Ltd., P.O.B. 164, Kibutz Horashim 45865, Israel.
7. Lock&Lock[®] boxes, supplied by S.D. Import & Marketing Household & Gift Ltd., 43 Ben Zvi St, Rishon LeZion 75146 Israel.

Metal Coupons

1. Silver, foil, 0.1 mm thick, 99.9% (metals basis), Sigma Aldrich Israel Ltd., Park Rabin, Rehovot 76100, Israel.
2. Copper foil, 0.254 mm thick, 99.9% (metals basis), Intrater Co., Lurie 5, Tel Aviv, Israel (produced by Alfa Aesar, UK).
3. Lead foil, 0.1 mm thick, 99.9% (metals basis), Intrater Co., Lurie 5, Tel Aviv, Israel (produced by Alfa Aesar, UK).

Test Setup

1. Erlenmeyer 250 ml glass vessels with ground glass stoppers: Duran Group GmbH, Hattenbergstrasse 10, 55122 Mainz, Germany.
2. Teflon ribbon: PTFE thread seal tape, conforms to BS7786:1995 Grade L, 0.075 mm, TBA Sealing Materials, UK.
3. Nylon monofilament: 0.30 mm, Harvest Brand Strong Fishing Lines.
4. Medical cotton wool: Fresh Ones, 100% pure perforated cotton, Yena Taasiyot Ltd., P.O. box 146, Ramle, Israel.
5. Alconox: Alconox, Inc., 30 Glenn Street, Suite 309, White Plains, New York 10603, USA.

Equipment

1. Model 5975 SMB ion source and interface (Aviv Analytical, Hod Hasharon Israel), installed on an Agilent GC-QQQ-MS system equipped with 7890A GC and with a 7000A Triple Quadruple Mass Spectrometer (QQQ-MS).
2. ClimaCell[®] cooling incubator with controlled humidity, MMM Medcenter, Einrichtungen GmbH, Schulstrasse 29, D-82166, Gräfelfing, Germany.
3. HRSEM imaging performed with FEI Sirion HR SEM, Eindhoven, Holland.

Chemicals

1. Activated carbon collectors: Charcoal activated (for gas chromatography) powder (35–50 mesh ASTM), Merck Millipore Ltd., Croxley Green Business Park, Watford, Hertfordshire, UK.
2. Acetone: Acetone AR, Gadot Group, 5 Hamelacha St., Haogen Building, P.O. Box 8751, 4250540 Netanya, Israel.
3. Ethanol: Ethanol absolute (dehydrated) AR-b, BioLab Ltd., P.O. Box 34038, Jerusalem 91340, Israel.
4. Alconox: Sigma Aldrich Israel Ltd., Park Rabin, Rehovot 76100, Israel.

APPENDIX C: METAL COUPONS

Purity and coupon size were selected in accordance with the Oddy test protocols formed by the Getty Institute (Schiro 2011), as follows:

1. Silver: new coupons, 99.9% purity, 10 × 15 mm, 0.1 mm thick.
2. Copper: new coupons, 99.9% purity, 10 × 15 mm, about 0.254 mm thick.
3. Lead: new coupons, 99.9% purity, 10 × 15 mm, 0.1 mm thick.

All metal coupons were cleaned first with a glass fiber bristle brush, then with MicroMesh® sanding cloth, followed by dipping in ethanol and finally in acetone.

APPENDIX D: ACTIVATED CARBON

The activated carbon used was charcoal activated for gas chromatography, 0.3–0.5 mm (35–50 mesh ASTM). Surface area and pore size of the activated carbon selected for use were determined by the N₂ Brunauer–Emmett–Teller (BET) method (NOVA1200e). BET surface area was 654 m²/g and the pore volume was 0.6 cm³/g.