

An unexpected danger with ISO16000 emission tests

David Thickett
Senior Conservation Scientist
National Collections
English Heritage





Species

- Acetic acid
- Formic acid
- Nitric acid
- Hydrogen sulfide
- Carbonyl sulfide
- Dimethyl sulfide
- Formaldehyde
- Acetaldehyde
- Styrene
- Ammonia
- Ethyl acetate
- Ethyl formate
- Ethyl propanate
- Methyl acetate
- Methyl propanate
- Vanillin
- Iso butyl benzol
- Hexanal
- 1,4 diethylbenzene
- Furfural
- Toluene
- 2 pentylfuran
- Diethylamine ethanol
- Octadecylamine
- Peroxyacetyl nitrate
- Chlorides (29% 200 Oddy Cu tests have Cl in corrosion product)
- Mercaptans
- Peroxides
- Fumigants
- Flame retardants



BEMMA assessment scheme



BEMMA: Assessment of emissions from materials for museum equipment

1. Methods of analysis

1. Micro chamber (μ -CTE)
2. DIN ISO 16000-6 (sample taking with Tenax®; VOCs, SVOCs; 0,25 liters withdrawal volume; 10 min)
3. DIN ISO 16000-3 (sample taking with DNPH- cartridges for aldehyde and ketone; VVOCs, VOCs, SVOCs)
4. Formic and acetic acid BAM specific analytic process referring to DIN ISO 16000-3; (derivating, LC-MS; 30 liters withdrawal volume; 20 h)
5. Iso-cyanate (derivatisation, HPLC; 15 liters withdrawal volume; 10 h)
6. Anorganic gases (sensors and optical measuring devices within the scope of 0 to 250 ppm)

2. Criteria

1. Substances with high contamination potential, such as formic acid, acetic acid, formaldehyde, H_2S , SO_2 , NH_3 ; 2,6-TDI, HDI, 2,4-TDI and oxime (s. table 2) must not be detectable
2. Sum emission figures for Σ VVOCs: $100 \mu g/m^3$, Σ VOCs: $500 \mu g/m^3$ with the exception of sealing materials with Σ VOCs: $2000 \mu g/m^3$ due to significantly smaller application surface, for Σ SVOCs: $100 \mu g/m^3$ and anorganic gases (planned)

BEMMA SCHEME

Emission figures (< detection limit) for substances with high contamination potential

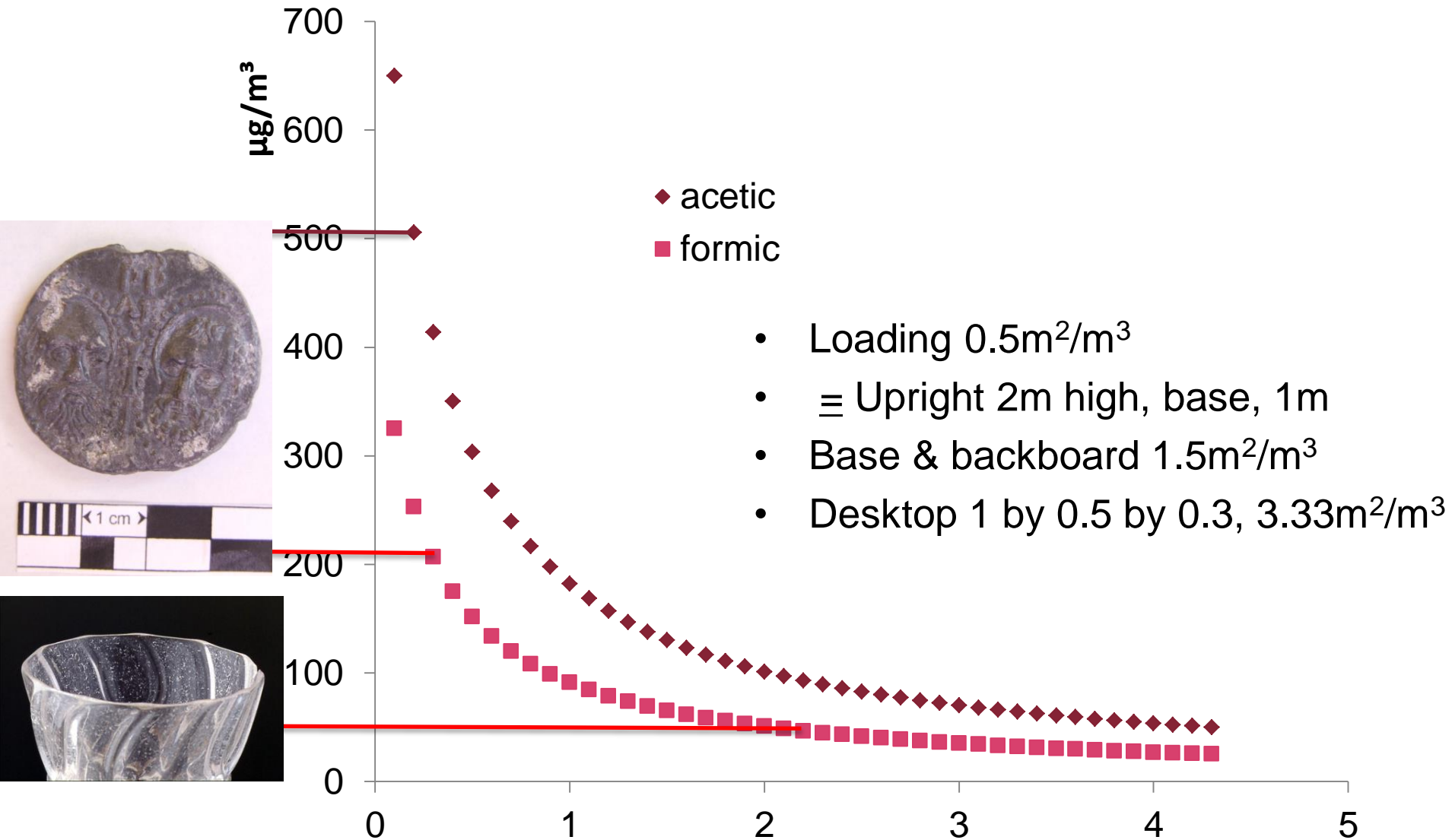
Substances:	Detection limit in µg/m³:	Analytic process
Formic acid	25	BAM specific process, referring to DIN ISO 16000-3
Acetic acid	50	BAM specific process, referring to DIN ISO 16000-3
Formaldehyde	2	DIN ISO 16000-3
2,6-TDI	2	OSHA ² method number 42 for DIISOCYANATES
HDI	2	OSHA ² method number 42 for DIISOCYANATES
2,4-TDI	1	OSHA ² method number 42 for DIISOCYANATES
Oxime	5 (Toluene equivalent)	DIN ISO 16000-6

Neither TDI nor MDI is generally **corrosive** towards **metals** (except aluminium).

Parameters

- BEMMA Oddy
- Volume 1m^3 0.00005
- Air exchange rate $0.18\text{ h}^{-1} \equiv 4.32\text{ d}^{-1}$ 0.034 d^{-1}
- Loading $0.5\text{m}^2/\text{m}^3$ 72
- Measured after 144h (20h BEMMA) 28 days
- Detection Limits
- $50\mu\text{g}/\text{m}^3$ acetic $2\mu\text{g}/\text{m}^3$
- $25\mu\text{g}/\text{m}^3$ formic $1\mu\text{g}/\text{m}^3$

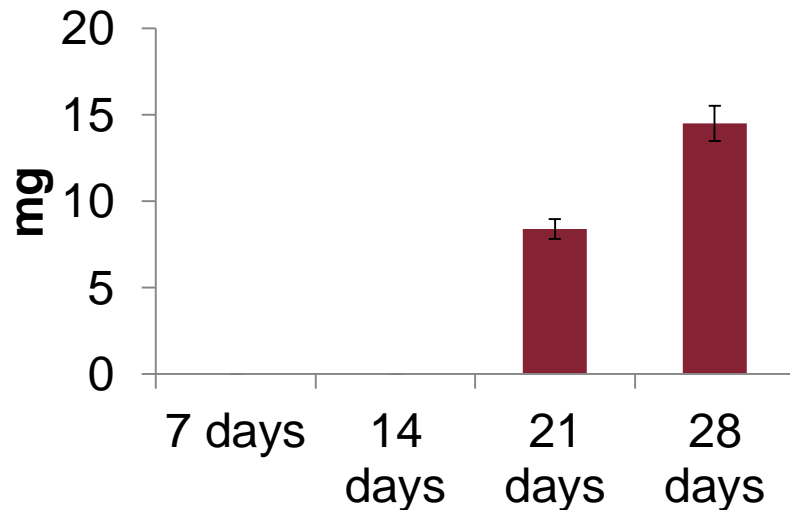
Meyer and Havermanns



Necessity of Accelerated Aging

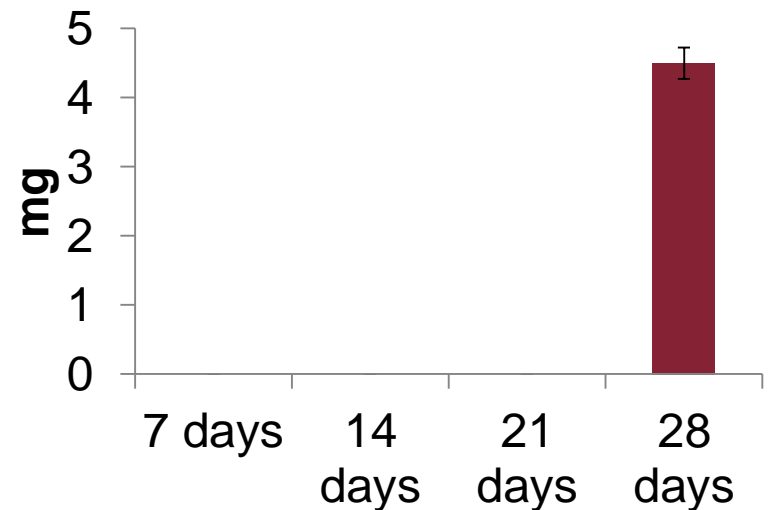
- 28 days always an issue, but species are degradation products
- Oddy tests weekly check, over 400, about 4%, late fails, 2% in last week of test
- Gas analysis

acetate



DL 0.005mg

nitrate

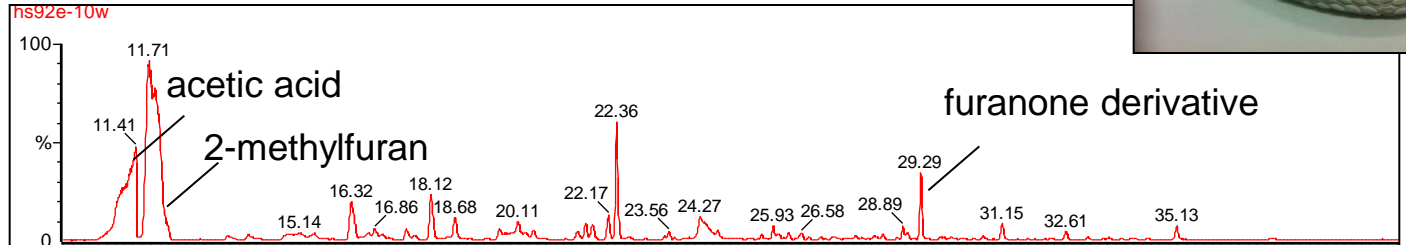


DL 0.001mg

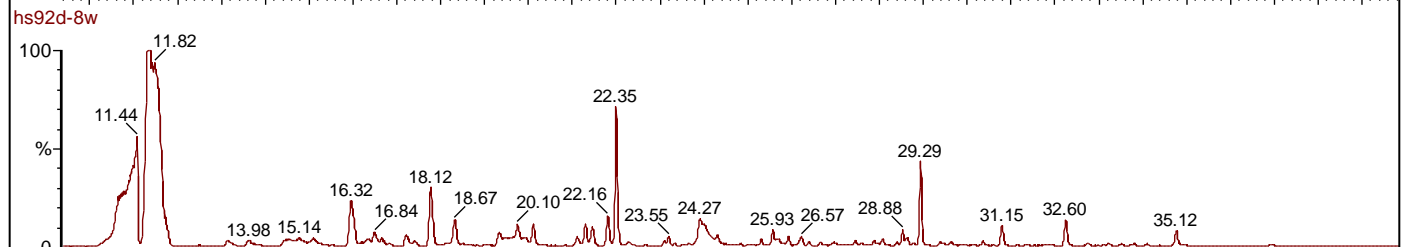
Degradation time
(80 ° C/60%RH)



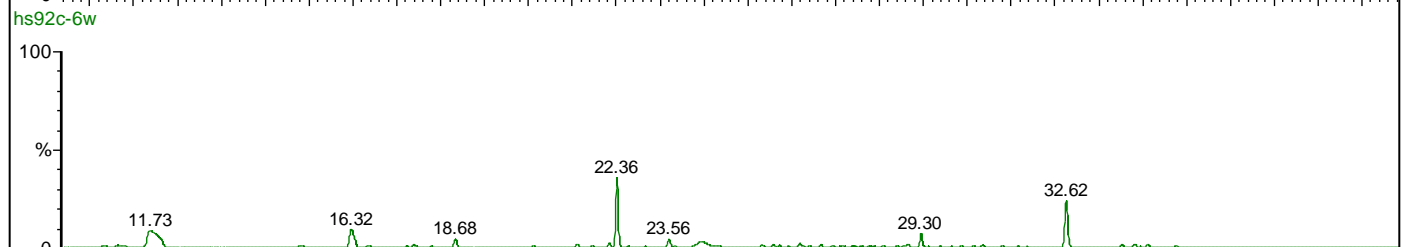
10 weeks



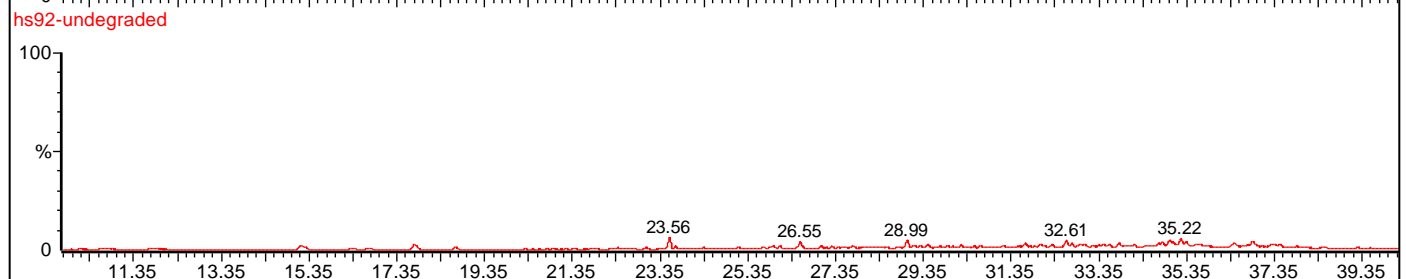
8 weeks



6 weeks

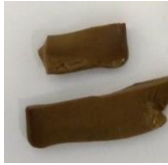


none



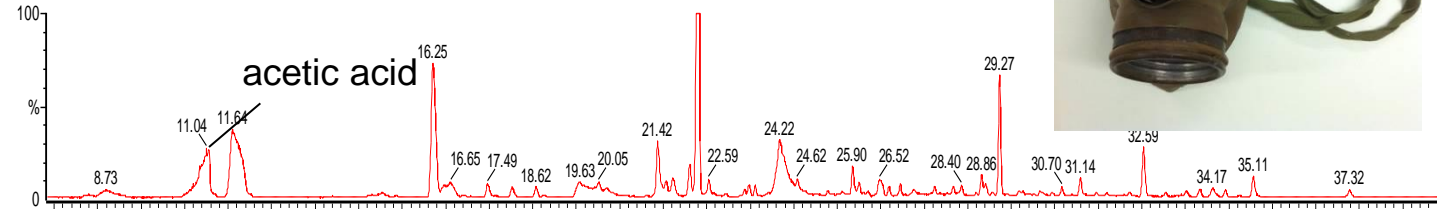
Degradation time
(80 ° C/60%RH)

10 weeks



HS87c Degraded 6W

hs87e degraded 10w 13-06-13



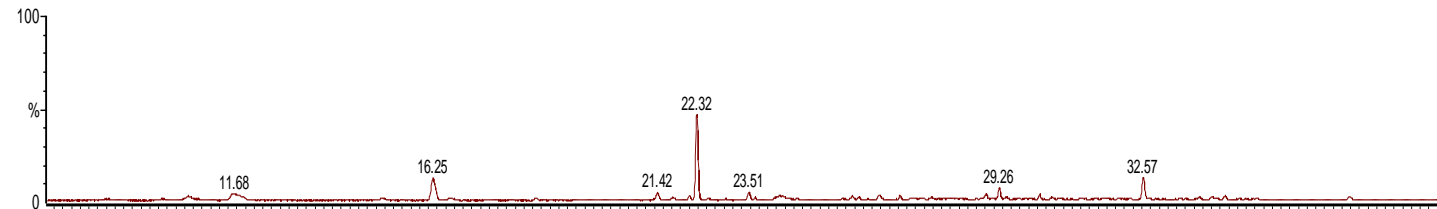
Combipal SPME,50/30umDVB/CAR/PDMS (graybrown gas mask)



8 weeks



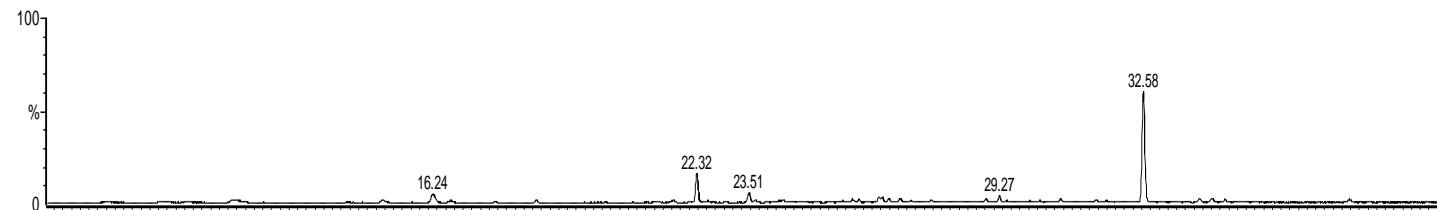
hs87d degraded 8w 13-06-13



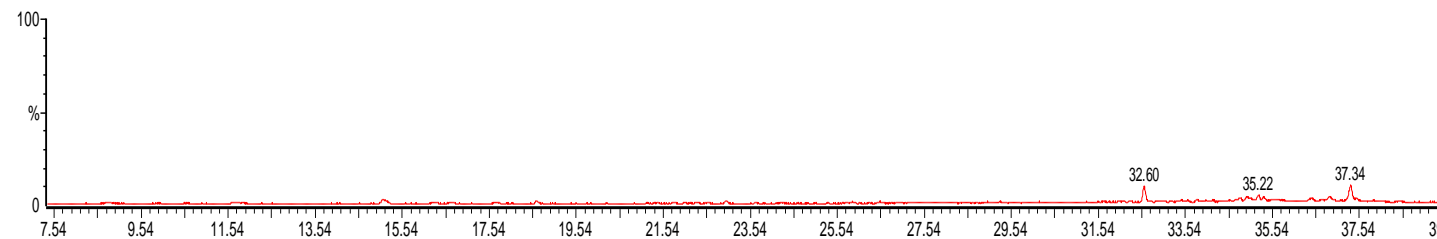
6 weeks



hs87c degraded 6w 13-06-13



hs87 undegraded 13-06-13



none

ODDY ISSUES

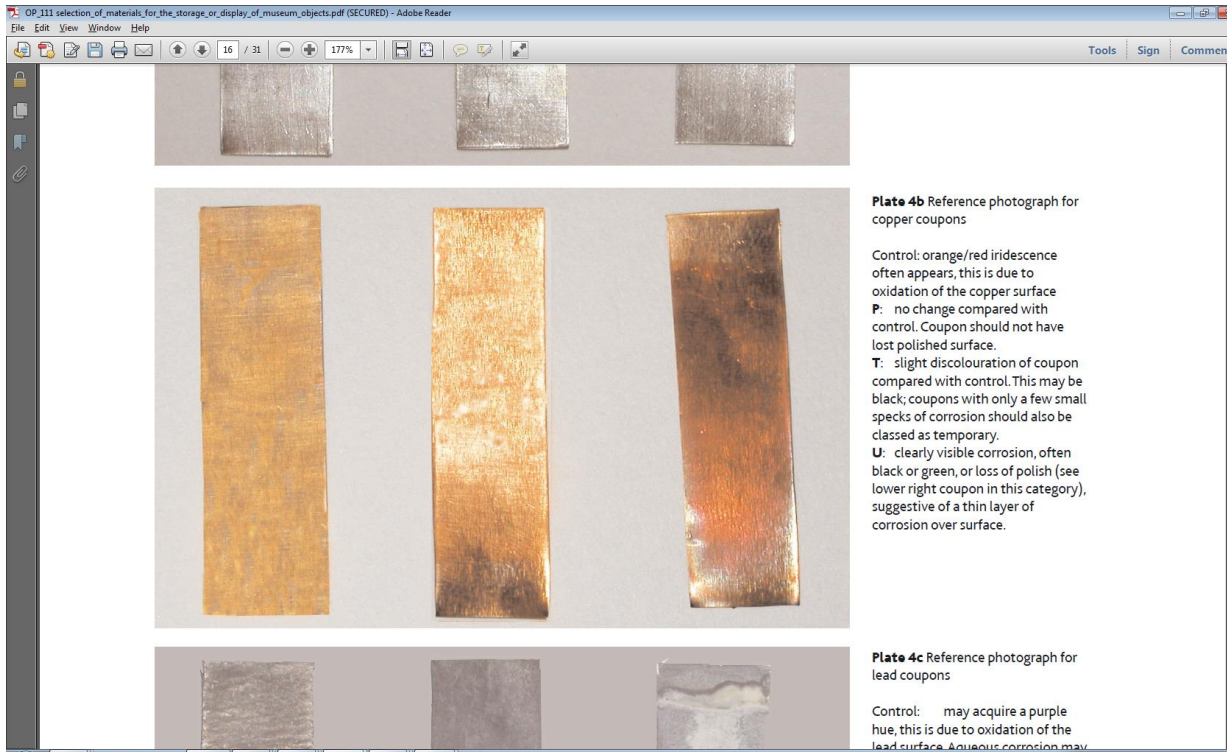
- **IF** follow method, accelerated corrosion tests can have low reproducibility
 - Two main areas;
 - Metal surface preparation
 - Assessment of coupons at end of test
- But overcome by other industries, ISO9223, 11844, electronics, silver coins/silverware
- **ONLY** metals, (Ag, Cu, Pb Fe, Zn, Sn, Cd, Al)
 - Extended to paper and silk,
 - working on bone and ivory

METAL PREPARATION

- Oddy (Robinet 2003)
 - GBBrush, Spectrosol acetone 1 min, damp tissue
- ISO 9223, ISO 11844,
ISA S.71.04-1985, ASTM G1-90: 1999
- Recent British Museum
 - Micromesh, alumina, Chromanorm acetone, Cl free tissue

ASSESSMENT - VISUAL

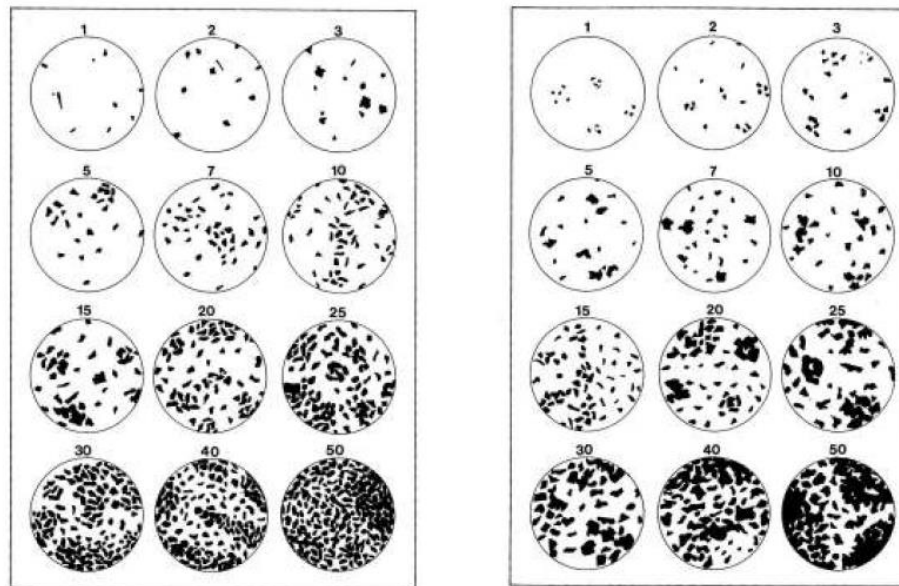
- Published guide photographs and descriptions



- Methods low tech dust kit, Regis Berthelon thesis

Adapt images and systemise

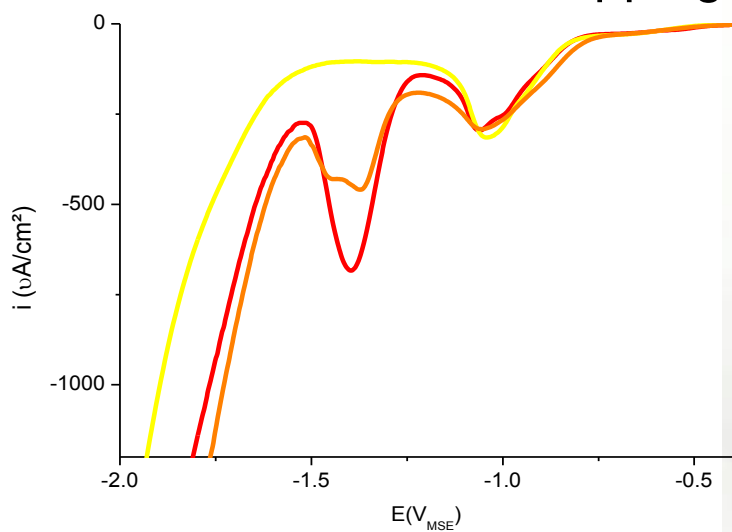
Covering: percentage



If the coverage is to be estimated, you could use a chart like those used in microscopic examination to estimate the percentage of grains or minerals.

ASSESSMENT – LOWER COST

- Colorimetry (Tetreault)
- Image analysis (Wang et al),
 - Image J, % and colour
 - Challenging for temporary
- Mass Gain
- Mass Loss (stripping)
- Electrochemical stripping



ASSESSMENT INSTRUMENTAL

- LEAD

- XRD
- FTIR

- PAPER

- Viscometry (DP)
- NIR
- FTIR
- Ion chromatography (low MW sugars)

- COPPER

- XRD
- FTIR
- SEM-EDAX

- SILVER

- Grazing angle XRD
- FTIR (sulfates, oxides)
- SEM-EDAX
- XRF
- XPS
- Static SIMS
- Dynamic SIMS

1000+ instances of corrosion investigated

material	corrosion	tested	new test		enviro data			
				T/RH	acetic/for SO, NO,	O3	other	
Cu alloy	copper hydroxide	no	fail copper	han 156				ammonia
			pass					
			fail lead					
			pass					
marble	calcium formate	no	fail lead	ACR 345	yes	yes	no	no
	calcium acetate							
Cu alloy	sodium copper acetate carbonate 1	no	fail lead	ACR 120	yes	no	no	no
	sodium formate		fail lead					
	sodium copper acetate carbonate 2							
lead	lead formate	fail lead	6 months fail lead					
glass	sodium formate	no	fail lead	han 12	yes	no	no	form, meth,eth
			fail lead					
glass	sodium formate	no	fail lead	han 13				form, meth,eth
			fail lead					
glass	sodium sulfate	no	fail lead, copper	han 57	yes	no	no	no
enamel	sodium formate	no	fail lead	after ACR184	yes	no	no	no
			fail lead					
			fail lead					
			fail lead					

File Home Insert Page Layout Formulas Data Review View Add-Ins Acrobat

Clipboard: Paste, Cut, Copy, Format Painter

Font: Arial, 10, Bold, Italic, Underline, Text Color, Background Color

Alignment: Left, Center, Right, Justify, Merge & Center

Number: General, Percentage, Decimals

Styles: Conditional Formatting, Format as Table, Cell Styles

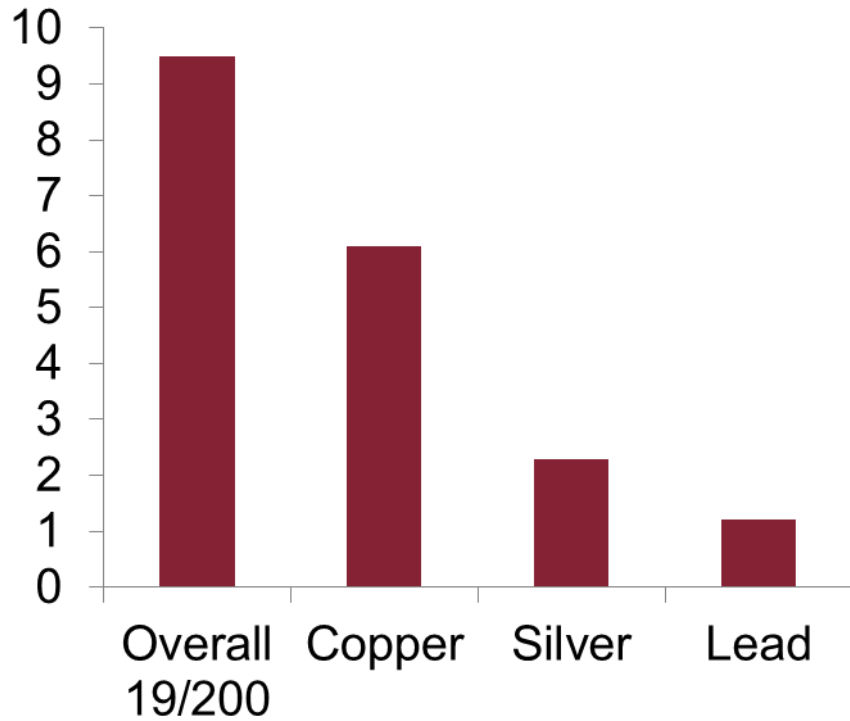
Cells: Insert, Delete, Format

AutoSum, Fill, Clear

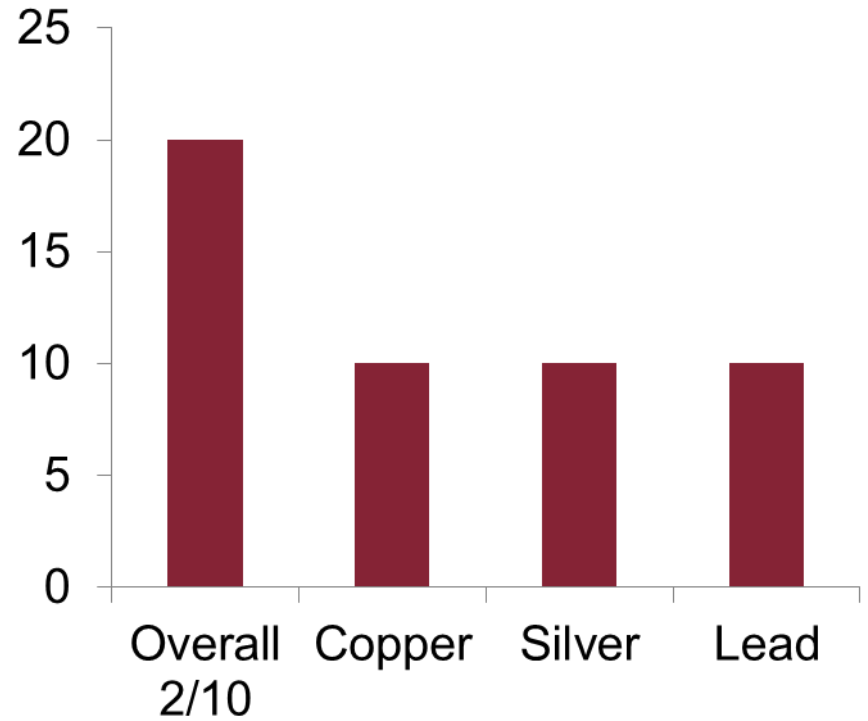
	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R
66	FABRIC	CUTE EUF	BEIGE		P	P	P					8.4						
67	FABRIC	SECTA CL	BEIGE;GREEN		P	P	P					6.1						
68	FABRIC	ONIVESC	BEIGE		P	P	P					6.6						
69	FABRIC	PANEIS A	BEIGE;GREEN		P	P	P					6.1						
70	FABRIC	FABRIC	BEIGE		P	P	P					6.7						
71	FABRIC	VITRINES	BEIGE		P	P	P					6.6						
72	PAINTED	WEATHEF	RED;BEIGE		P	P	P					8.5						
73	FABRIC	BRANSCC	GREEN	JO124-780	P	P	P					6.2						
74	FABRIC	TRUE COL	YELLOW	AL6302/79	P	P	P					5.3						
75	FABRIC	TRUE COL	YELLOW	AL6302/80	P	P	P					5.3						
76	FABRIC	SONATA	GREEN	306	P	P	P					6.7						
77	FABRIC	CASCADE	YELLOW	102	P	P	P					6.1						
78	FABRIC	MARATI	RED	19-Nov	P	P	P					6						
79	FABRIC		GREEN		P	P	P					6.3						
80	FIBRE	FELT	GREY;GREEN;PALE		P	P	P					5.7						
81	FABRIC	CHINTZ	PINK	6000/9024	P	P	P					0						
82	FABRIC	BOMULSA	PINK	373	P	P	P					0						
83	FABRIC	TRUE COL	GREEN D,	AL6302/67	P	P	P					5.6						
84	FABRIC	BRANSCC	BLUE	JO1024-61	P	P	P					8.2						
85	FABRIC	BRANSCC	BLUE	JO1024-64	P	P	P					6						
86	FABRIC	BRANSCC	GREEN	JO1024-77	P	P	P					6.1						
87	PAPER	ACID FRE	WHITE		P	P	P					6.5						
88	FABRIC	INDIANA	GREY	16	P	P	P					5.6						
89	FABRIC	VELVET	BLUE		P	P	P					0						
90	FABRIC	ULTRA II	PURPLE	207	P	P	P					6.7						
91	FABRIC	ULTRA II	PURPLE;F	208	P	P	P					6.6						
92	FABRIC	NORMANI	GREY;CLAY		P	P	P					6.5						
93	FABRIC	HAMILTON	BEIGE		P	P	P					8.1						
94	FABRIC	RELAXED	GREY;SLA	7900-09	P	P	P					7.3						
95	FABRIC	EMPORIO	BEIGE	14672	P	P	P					6.3						

Direct contact extra risk

Fabrics

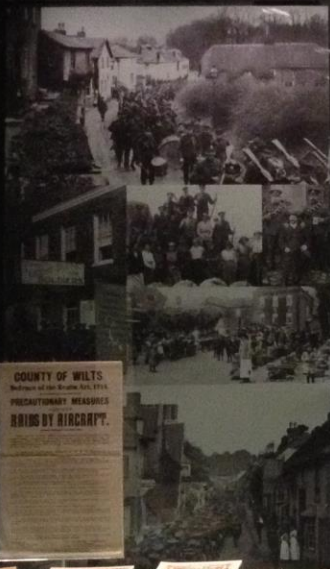


Powder Coatings

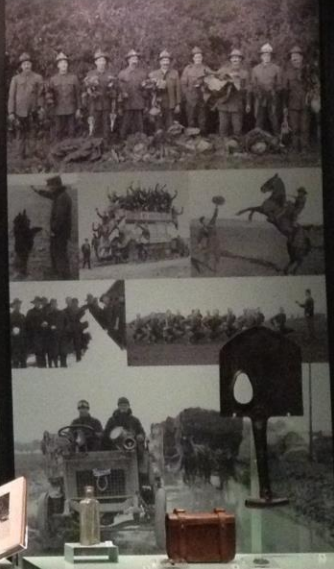
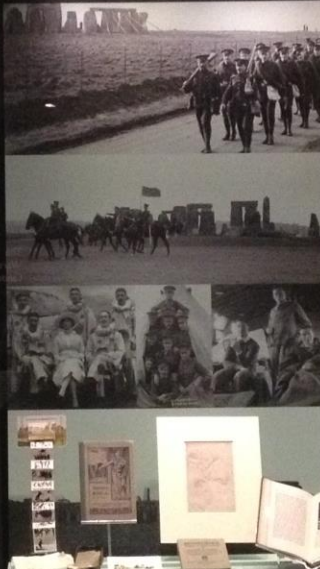


New materials

- Paper, (Strlic et al 2011)
 - Viscometry, fiddly
 - NIR (Surv NIR) possible
 - FTIR calibration as widely available in museum and science labs
- Silk, (Luxford 2009)
 - NIR
 - FTIR methods published
- Differential for organic materials less, need decide acceptable
 - At 50%RH, 20C, 1000 $\mu\text{g}/\text{m}^3$ acetic
 - lead no corrosion to 4g/m²
 - Paper DP half life decreases by approx 10%



COUNTY OF WILTS.
Before and After.
PRECAUTIONARY MEASURES
TAKING BY AIRCRAFT.



Living in the Camps

A great change is going to take place in our life, our quiet village is to be inundated and we are to have a camp of 4,000 soldiers settled down on Sandhill. Shree fellow we shall be no longer. We are going to learn the lesson of our lives.

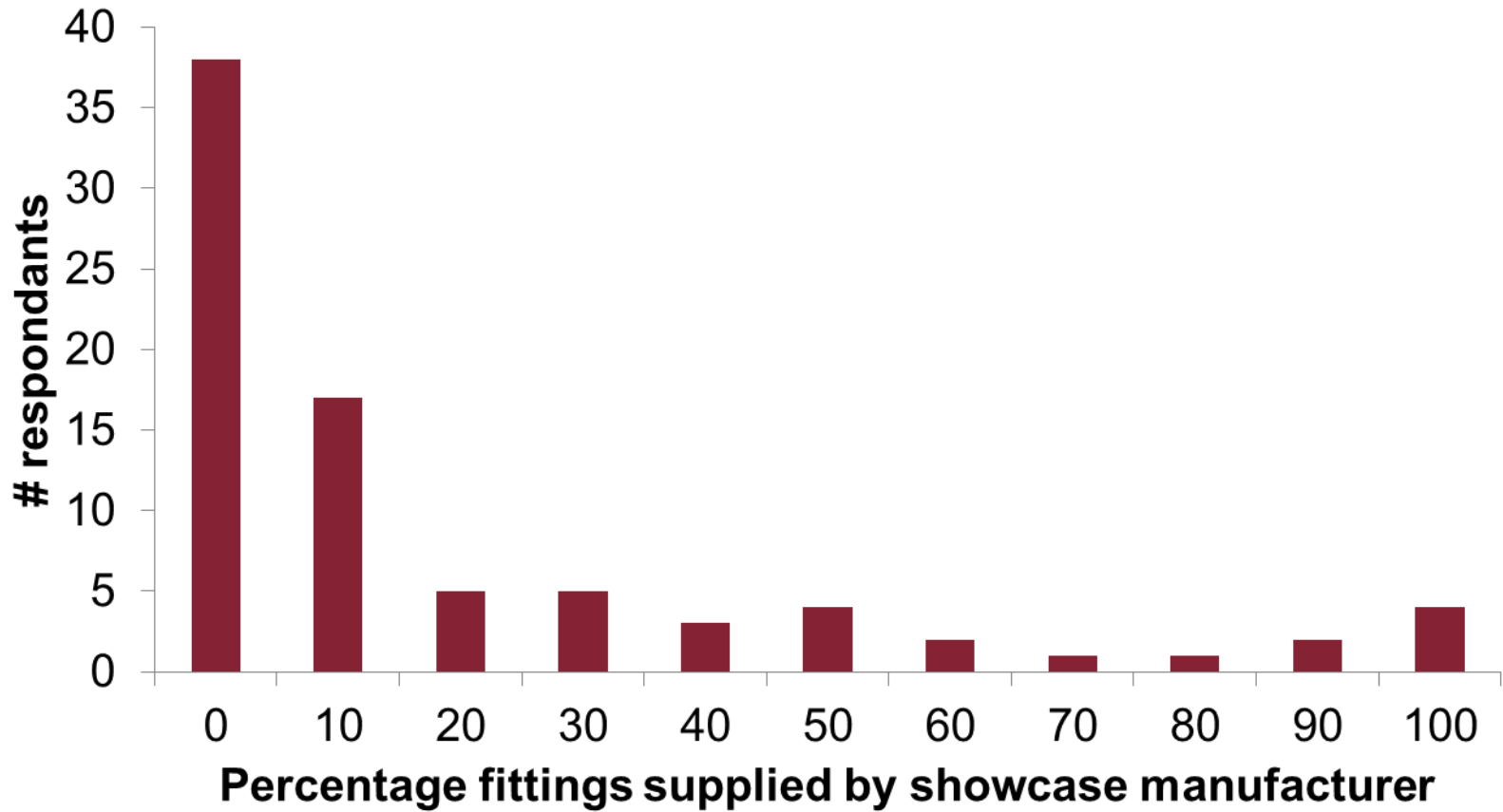
For the soldiers who came to this camp, we was often hard and monotonous. Army routine and discipline meant a lack of freedom and privacy.

All King's men's methods were quickly rejected, taking uniforms or given their own existing capotes. When Cavalian troops arrived they had to live in tents because there were too few huts. Six in the early years of the war those who had accustomed to do their job were more willing to put up with their conditions.

For most people the camps were both a blessing and a curse. Although they received the food, clothing these were free of dampness, wind and rain.



SURVEY RESULTS – James Crawford



CONCLUSIONS

- As profession need to decide way forward
 - ISO 16000, species, unknown species, late emission of degradation products
 - levels, conditions
 - Oddy, need tighten up and develop method
 - Probably a method that's less accessible
 - Oddy has degree of flexibility, new materials, direct contact

Acknowledgements

- Kathryn Curran, UCL institute for Sustainable Heritage
- James Crawford, University of Warwick
- Virginia Costa, Federal University, Porto Alegre, Brazil
- Naomi Luxford, English Heritage
- Ana Marques, University of Porto/English Heritage
- Matija Strlic, UCL institute for Sustainable Heritage
- Michel Dubois, CNRS
- David McPhail, Imperial College

