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*Supplementary Materials*

# Oxygen Depletion Testing of Metals

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## Supplementary Section S1

Schematics for experimental equipment, Figures S1–S6, where:

- Research into preventative conservation:
  - Method (i) – Oxygen consumption and hydrogen evolution test
  - Method (ii) – Oxygen depletion test with glycerol to control the relative humidity
  - Method (iii) – Oxygen depletion test with silica gel to control the relative humidity
- A screening technique for archaeological iron and copper alloy stability:
  - Method (iv) – Display object deterioration survey
  - Method (v) – Dense Product Layer test
- A detection method for accelerated corrosion tests, such as the Oddy test:
  - Method (vi) – Oddy-type test

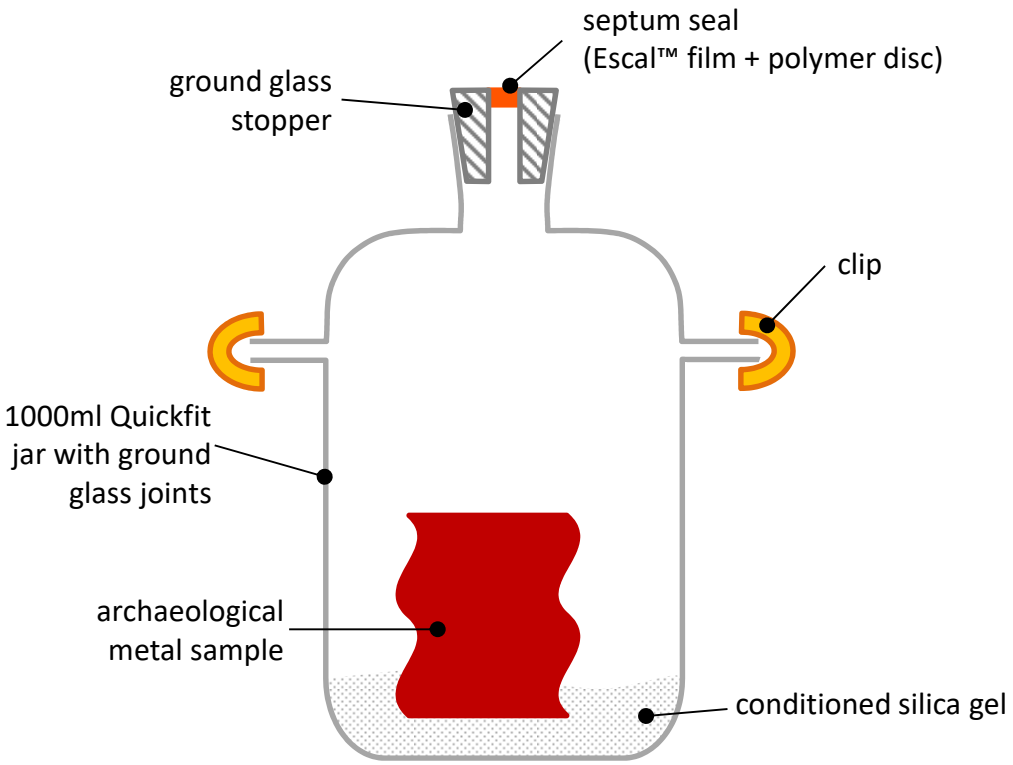


**Figure S1.** Method (i): Oxygen consumption and hydrogen evolution test.

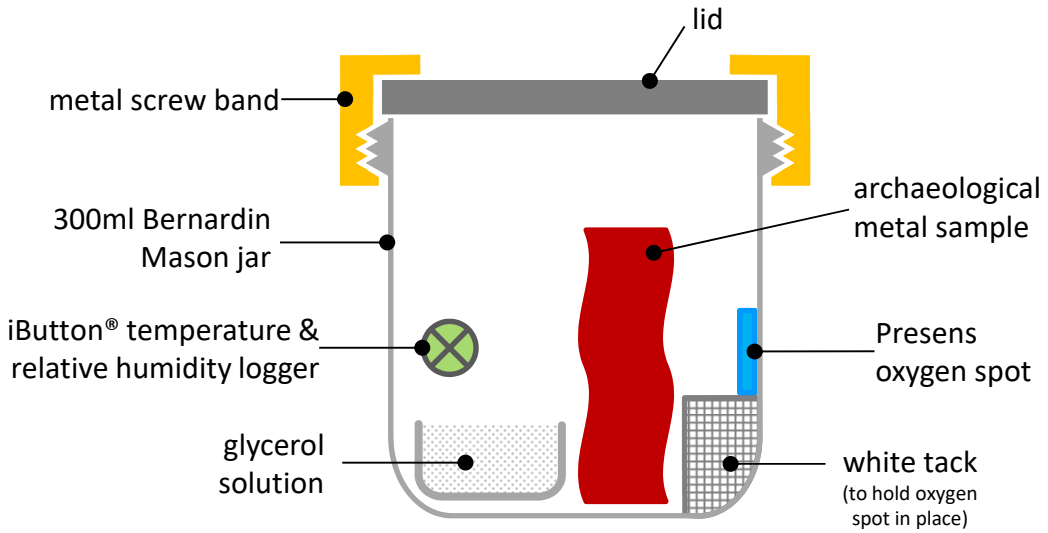


**Figure S2**. Method (ii): Oxygen depletion test with glycerol to control the relative humidity.

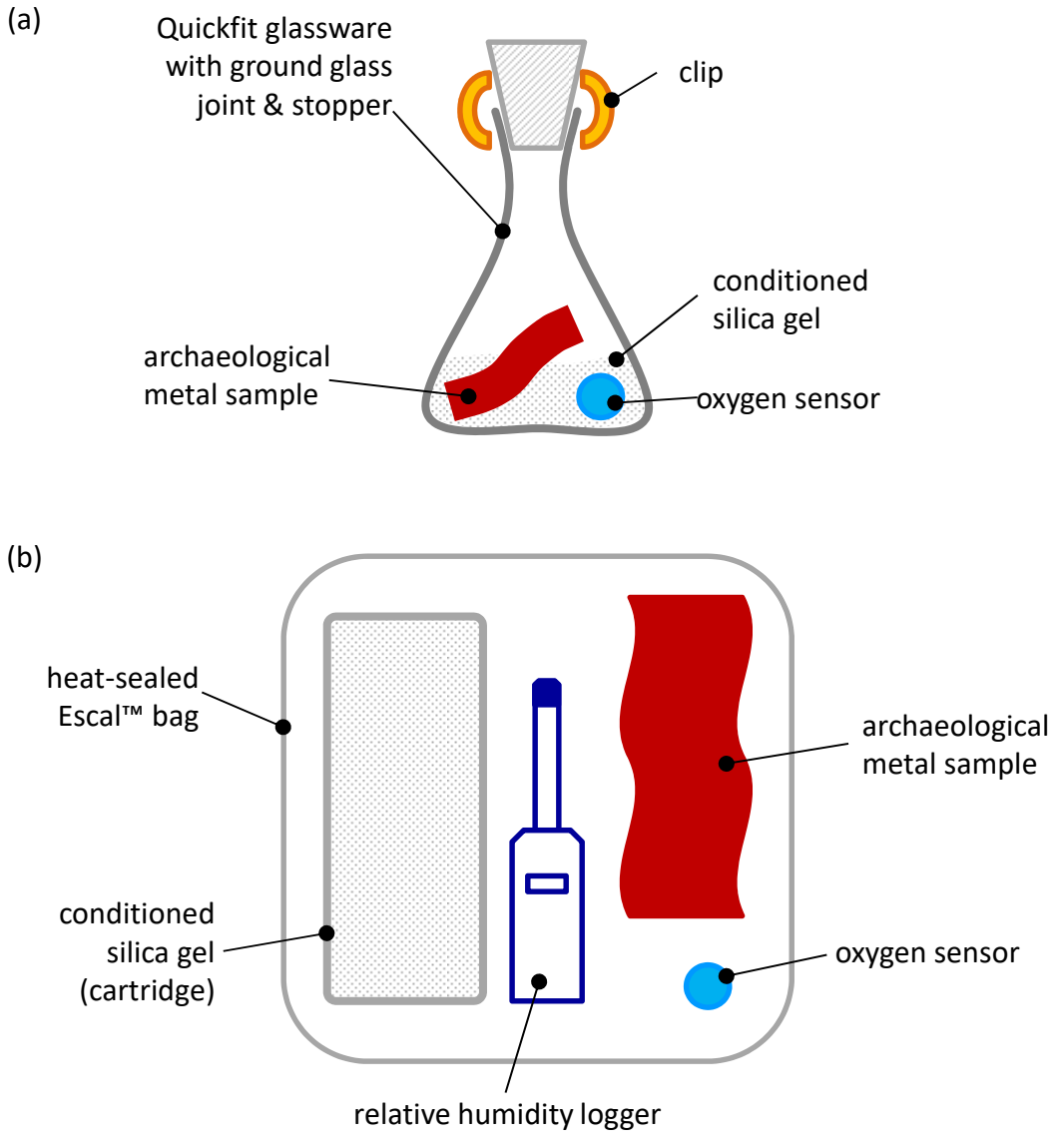

**Figure S3.** Method (iii): Oxygen depletion test with silica gel to control the relative humidity for (a) small and (b) large object dimensions.

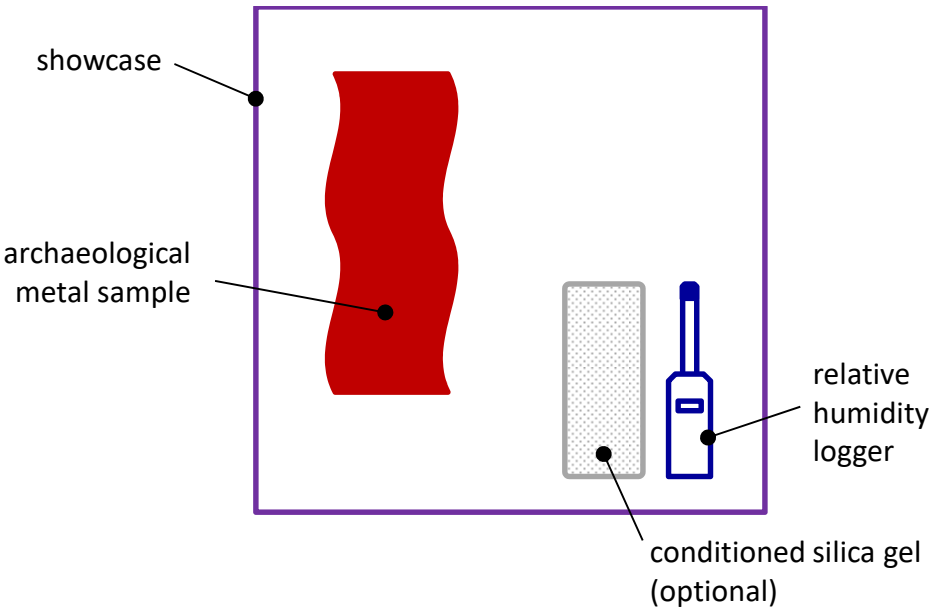


**Figure S4.** Method (iv): Display object deterioration survey.

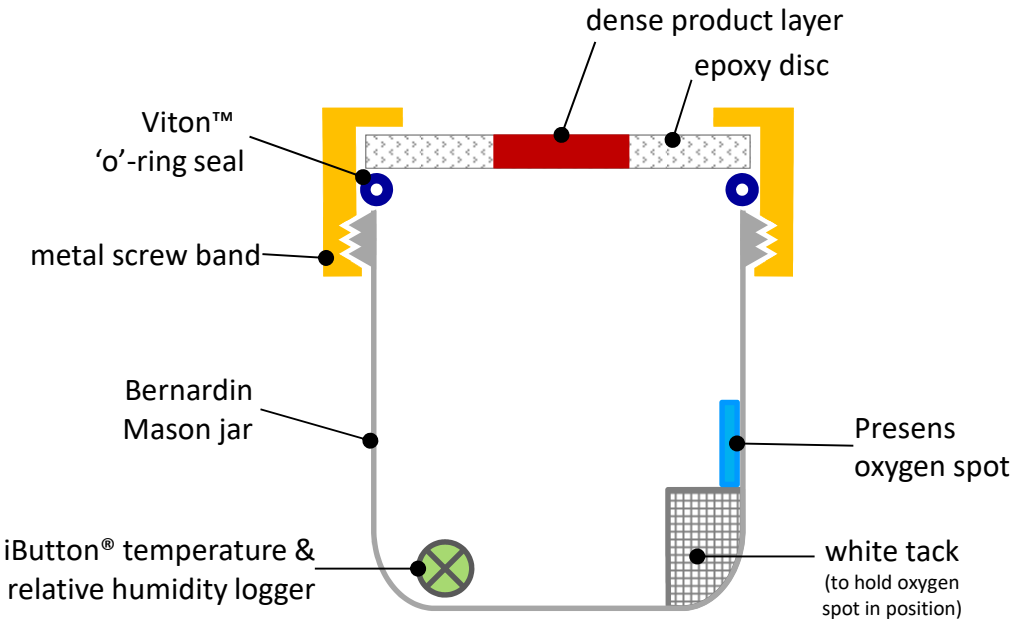


**Figure S5.** Method (v): Dense Product Layer test.

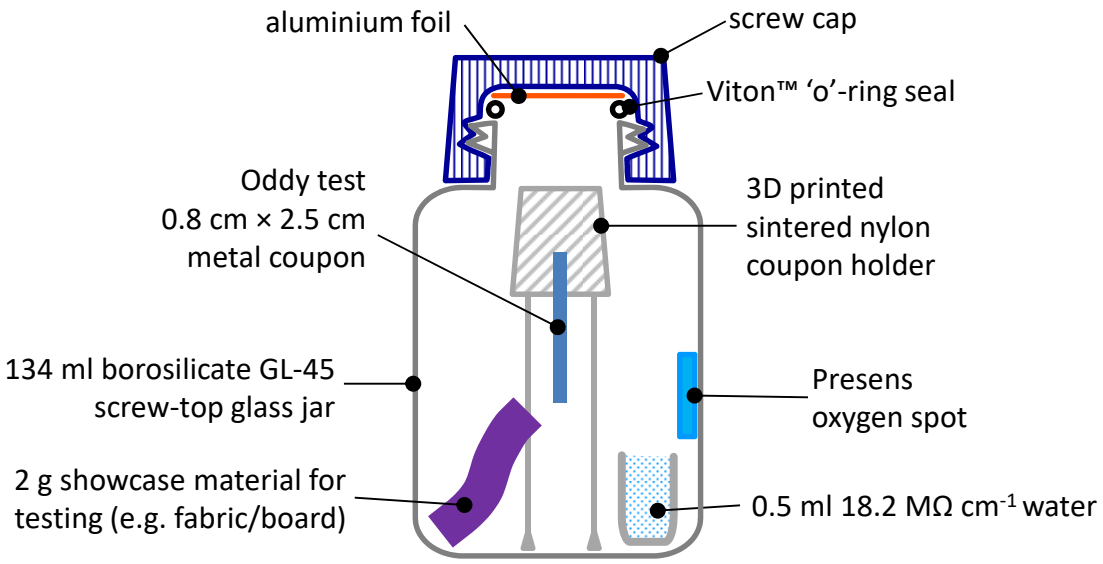


**Figure S6.** Method (vi): Oddy-type test. Note - One test for each metal had three Presens oxygen spots at different heights (top, middle, bottom) to check no concentration gradients were formed.

## Supplementary Section S2

Raw Data for all Figures, Tables S1–S7.

**Table S1.** For Figure 1: Oxygen depletion rates (mbar/yr/g) for selected samples examined at 20, 30, 40 and 50% relative humidity. Interquartile ranges and minimum and maximum values are shown. Excavated samples are from Caerleon (CPF, data taken from Watkinson et al. (2019)), Camber Castle (Cam) and Stonea (Stn).

| **Oxygen depletion rate (mbar/yr/g)** | **Sample** | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | **CPF20** | **Stn20** | **Cam20** | **CPF30** | **Stn30** | **Cam30** | **CPF40** | **Stn40** | **CPF50** | **Stn50** |
| Minimum | 0.40 | 0.00 | 0.00 | 0.10 | 0.00 | 5.23 | 1.62 | 0.00 | 2.06 | 0.00 |
| Lower quartile | 0.51 | 0.00 | 0.00 | 0.30 | 0.25 | 6.32 | 2.20 | 1.68 | 3.41 | 3.52 |
| Median | 0.75 | 0.00 | 0.00 | 0.51 | 0.58 | 6.85 | 2.93 | 2.49 | 4.06 | 5.56 |
| Upper quartile | 0.85 | 0.00 | 0.00 | 0.65 | 0.79 | 9.34 | 3.49 | 3.08 | 5.15 | 6.78 |
| Maximum | 1.05 | 0.00 | 0.00 | 0.81 | 0.89 | 11.54 | 4.81 | 5.09 | 5.90 | 8.12 |

**Table S2.** For Figure 2: Oxygen depletion rate ranges (mbar/yr/g) measured at 50% RH for selected samples. Solid data are from English Heritage, hatched data is from Watkinson *et al*. (2019); note Camber Castle data was only collected at 30% RH as this already showed corrosion – as illustrated in Figure 1.

| Location | Oxygen depletion rate range (mbar/yr/g) | | | | | | |
|---|---|---|---|---|---|---|---|
| | 0 | 0.3 - 2 | 2 - 4 | 4 - 6 | 6 - 8 | 8 - 10 | 10 - 12 |
| **Whitby Abbey** | 44.4 | | 11.1 | 29.7 | 14.8 | | |
| **Haughmond Abbey** | 39.1 | | 9.5 | 38.1 | 13.3 | | |
| **Dover Castle** | 30 | | 15 | 20 | 30 | 5 | |
| **Carisbroke Castle** | 33 | | | 41 | 26 | | |
| **Lullingstone Villa** | 56 | | | 25 | 8 | 11 | |
| **Pevensy Castle** | 42 | | 21 | 30 | 7 | | |
| **St Augustines Abbey** | 54 | | | 7 | 18 | 15 | 6 |
| **Stonea** | 42 | | | 32 | 16 | 10 | |
| **Uley** | 67 | | | | 8 | 13 | 12 |
| **Sutton Hoo** | 52 | | 12 | 18 | 10 | 8 | |
| **Billingsgate** | | 100 | | | | | |
| **Caerleon** | | | 38.5 | 53.8 | 7.7 | | |
| **Camber Castle (30% RH)** | | | | 5 | 42 | 45 | 8 |

**Table S3.** For Figure 3: Selected samples from Sutton Hoo (SH) showing oxygen consumption and hydrogen evolution characteristics.

| time (days) | Sample | | | | | |
|---|---|---|---|---|---|---|
| | Oxygen consumed (%) | | | Hydrogen evolved (%) | | |
| | SH1 | SH2 | SH3 | SH1 | SH2 | SH3 |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 1 | 0.4 | 0 | 0 | 0 | 0.19 | 0.05 |
| 3 | 0.8 | 0 | 0 | 0 | 0.51 | 0.16 |
| 7 | 1.1 | 0 | 0 | 0 | 0.61 | 0.43 |
| 14 | 1.7 | 0 | 0 | 0 | 0.87 | 0.55 |
| 21 | 2.65 | 0 | 0 | 0 | 1.13 | 0.7 |

**Table S4.** For Figure 4: Deterioration categorisation of over 1000 English Heritage archeological metal objects on display with respect to the maximum relative humidity ranges that they have experienced.

| Maximum relative humidity experienced (%) | Deterioration categorisation | | | |
|---|---|---|---|---|
| | none | slight | medium | heavy |
| 20-30 | 392 | | | |
| 30-40 | 147 | 40 | 3 | 8 |
| 40-50 | 56 | 45 | 2 | 13 |
| 50-60 | 42 | 35 | 17 | 14 |
| 60-70 | 32 | 43 | 8 | 12 |
| 70-80 | 26 | 39 | 30 | 6 |

**Table S5.** For Figure 5: Amount of oxygen and water vapour penetrating dense product layer samples after 14 days.

| Sample | Oxygen Concentration (%) | Relative Humidity (%) |
|---|---|---|
| A | 8.9 | 33.1 |
| B | 6.7 | 21.7 |
| C | 11.2 | 34.3 |
| D | 18.6 | 45.3 |
| E | 10.1 | 32.0 |
| F | 6.3 | 19.2 |
| G | 17.1 | 49.8 |
| H | 17.3 | 48.1 |

**Table S6.** For Figure 6: Accelerated ageing Oddy tests for (a) lead (Pb), (b) copper (Cu), (c) silver (Ag) and (d) steel (Fe) showing results for 32 individual samples (8 samples per Oddy test) as metal corrosion mass loss (mg/cm2 ± 0.01 or μg/cm2 ± 0.01) and % oxygen depletion (± 0.1%); error bars are shown.

| Oddy test metal | Sample | Mass loss – Pb ($mg/cm^2$) | Oxygen depletion (%) |
|---|---|---|---|
| Lead (Pb) | 1 | 0.02 | 0.02 |
| Lead (Pb) | 2 | 0.08 | 0.23 |
| Lead (Pb) | 3 | 2.6 | 1.2 |
| Lead (Pb) | 4 | 5.3 | 2.6 |
| Lead (Pb) | 5 | 7.6 | 3.7 |
| Lead (Pb) | 6 | 17.8 | 9.2 |
| Lead (Pb) | 7 | 26.4 | 14.2 |
| Lead (Pb) | 8 | 42.6 | 20.8 |

| Oddy test metal | Sample | Mass loss – Cu(I) ($mg/cm^2$) | Mass loss – Cu(II) ($mg/cm^2$) | Oxygen depletion (%) |
|---|---|---|---|---|
| Copper (Cu) | 9 | 0.01 | 0.03 | 0.01 |
| Copper (Cu) | 10 | 0.01 | 0.01 | 0.05 |
| Copper (Cu) | 11 | 0.1 | 0.2 | 0.24 |
| Copper (Cu) | 12 | 0.2 | 0.5 | 0.73 |
| Copper (Cu) | 13 | 0.7 | 0.4 | 1.54 |
| Copper (Cu) | 14 | 0.4 | 0.9 | 2.12 |
| Copper (Cu) | 15 | 2.2 | 1.3 | 4.7 |
| Copper (Cu) | 16 | 4.5 | 1.2 | 8.4 |

| Oddy test metal | Sample | Mass loss – $Ag_2S$ ($\mu g/cm^2$) | Mass loss – AgO ($\mu g/cm^2$) | Oxygen depletion (%) |
|---|---|---|---|---|
| Silver (Ag) | 17 | 2 | 0.5 | 0.01 |
| Silver (Ag) | 18 | 3 | 1.1 | 0.01 |
| Silver (Ag) | 19 | 9 | 0.05 | 0.06 |
| Silver (Ag) | 20 | 12 | 0.3 | 0.03 |
| Silver (Ag) | 21 | 17 | 0.1 | 0.04 |
| Silver (Ag) | 22 | 19 | 0.6 | 1.23 |
| Silver (Ag) | 23 | 23 | 1.2 | 2.12 |
| Silver (Ag) | 24 | 45 | 1.1 | 0.2 |

| Oddy test metal | Sample | Mass loss – Fe ($mg/cm^2$) | Oxygen depletion (%) |
|---|---|---|---|
| Steel (Fe) | 25 | 0.88 | 1.3 |
| Steel (Fe) | 26 | 0.95 | 1.5 |
| Steel (Fe) | 27 | 1.13 | 1.7 |
| Steel (Fe) | 28 | 1.23 | 1.8 |
| Steel (Fe) | 29 | 3.98 | 6.5 |
| Steel (Fe) | 30 | 4.25 | 6.8 |
| Steel (Fe) | 31 | 4.75 | 7.0 |
| Steel (Fe) | 32 | 5.07 | 7.5 |

**Table S7.** For Figure 7: Correlation of oxygen depletion versus total mass loss for the four types of accelerated ageing Oddy test: (a) lead (Pb), copper (Cu) and steel (Fe), (b) silver (Ag).

| Oddy test metal | Sample | Total mass loss ($mg/cm^2$) | Oxygen depletion (%) |
|---|---|---|---|
| Lead (Pb) | 1 | 0.02 | 0.02 |
| Lead (Pb) | 2 | 0.08 | 0.23 |
| Lead (Pb) | 3 | 2.6 | 1.2 |
| Lead (Pb) | 4 | 5.3 | 2.6 |
| Lead (Pb) | 5 | 7.6 | 3.7 |
| Lead (Pb) | 6 | 17.8 | 9.2 |
| Lead (Pb) | 7 | 26.4 | 14.2 |
| Lead (Pb) | 8 | 42.6 | 20.8 |

| Oddy test metal | Sample | Total mass loss (mg/cm²) | Oxygen depletion (%) |
|---|---|---|---|
| Copper (Cu) | 9 | 0.04 | 0.01 |
| Copper (Cu) | 10 | 0.02 | 0.05 |
| Copper (Cu) | 11 | 0.3 | 0.24 |
| Copper (Cu) | 12 | 0.7 | 0.73 |
| Copper (Cu) | 13 | 1.1 | 1.54 |
| Copper (Cu) | 14 | 1.3 | 2.12 |
| Copper (Cu) | 15 | 3.5 | 4.7 |
| Copper (Cu) | 16 | 5.7 | 8.4 |

| Oddy test metal | Sample | Total mass loss (μg/cm²) | Oxygen depletion (%) |
|---|---|---|---|
| Silver (Ag) | 17 | 2.5 | 0.01 |
| Silver (Ag) | 18 | 4.1 | 0.01 |
| Silver (Ag) | 19 | 9.05 | 0.06 |
| Silver (Ag) | 20 | 12.3 | 0.03 |
| Silver (Ag) | 21 | 17.1 | 0.04 |
| Silver (Ag) | 22 | 19.6 | 1.23 |
| Silver (Ag) | 23 | 24.2 | 2.12 |
| Silver (Ag) | 24 | 46.1 | 0.2 |

| Oddy test metal | Sample | Total mass loss (mg/cm²) | Oxygen depletion (%) |
|---|---|---|---|
| Steel (Fe) | 25 | 0.88 | 1.3 |
| Steel (Fe) | 26 | 0.95 | 1.5 |
| Steel (Fe) | 27 | 1.13 | 1.7 |
| Steel (Fe) | 28 | 1.23 | 1.8 |
| Steel (Fe) | 29 | 3.98 | 6.5 |
| Steel (Fe) | 30 | 4.25 | 6.8 |
| Steel (Fe) | 31 | 4.75 | 7.0 |
| Steel (Fe) | 32 | 5.07 | 7.5 |

## Reference

Watkinson, D.E.; Rimmer, M.B.; Emmerson, N.J. The Influence of Relative Humidity and Intrinsic Chloride on Post-excavation Corrosion Rates of Archaeological Wrought Iron, *Studies in Conservation*, **2019**, *64:8*, 456-471. doi:10.1080/00393630.2018.1565006