Probing beneath the surface without a scratch
A *non-destructive* method for bulk elemental analysis

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Outline

- Introduction to Negative Muons
- Depth Profiling
- Recent Examples
- Conclusions
Elemental analysis

- Determine the composition of a material

- Techniques commonly used are:
  - X-Ray fluorescence
  - Scanning tunnelling microscope
  - Laser ablation
  - Mass spectrometry
  - Neutrons

- Some techniques are destructive

- Some are only surface sensitive
Different probes ‘see’ materials differently, complementary.
Muon properties

- fundamental, charged particles (+ and -)
- heavy electrons
- spin 1/2
- magnetic moment $3.2 \times m_p$
- mass $0.11 \times m_p$
- produced from pion decays
- lifetime $2.2 \ \mu s$
- decay into a positron or electron (+ $2\nu$)
Negative muons - usage

Diverse science areas

- Cultural Heritage
  - Bronze Age artefacts
  - Mary Rose artefacts
  - Swords
  - Cannon Balls
  - Sundials
  - Coins
- Solar cells
- Piezoelectric devices
- Li batteries
- Advanced engineering
- High Energy X-rays emitted
- Energy dependent of the atom which captures the muon
- 0.01-6 MeV – mass of the muon is 200x that of the electron
- High Energy X-rays emitted
  - 0.01 - 6 MeV
- Energy dependent of the atom which captures the muon
- Transition Energies are known from measurement and calculation
- **High Energy X-rays emitted**
  - 0.01 - 6 MeV

- **Energy dependent of the atom which captures the muon**

- **Transition Energies are known from measurement and calculation**
All peaks seen and should be used in identifying elements
All peaks help in identification

Peaks from different transitions can overlap
Development Setup

- Ge X-ray detector 0.1-10 MeV
- Low Energy Ge X-ray detector
- μ beam

Sample position

Electron counters
Depth Profiling - Simulations

ION RANGES

- Ion Range = 12.4 um
  - Straggle = 5.10 um
  - Skewness = 0.0795
  - Kurtosis = 3.1101

Layer 2  | Layer 3  | Layer 4

0 A  | Target Depth | 2.5 mm
Depth Profiling - Simulations

ION RANGES

- Ion Range = 196. um
- Straggle = 16.8 um
- Skewness = -2.5653
- Kurtosis = 22.8019

0 A - Target Depth - 2.5 mm
Depth Profiling - Simulations

ION RANGES

Ion Range = 413. um
Straggle = 29.0 um
Skewness = -3.0015
Kurtosis = 29.6929

(ATOMS/cm^3) / (ATOMS/cm^2)

Layer 2
Layer 3
Layer 4
0 A - Target Depth - 2.5 mm
ION RANGES

Ion Range = 757. um
Straggle = 56.3 um
Skewness = -2.9827
Kurtosis = 26.6006
Depth Profiling - Simulations

ION RANGES

Ion Range = 1.19 mm
Straggle = 67.9 um
Skewness = -3.5867
Kurtosis = 37.6314
Depth Profiling - Simulations

ION RANGES

- Ion Range = 1.69 mm
- Straggle = 94.5 um
- Skewness = -3.8395
- Kurtosis = 43.0971

(ATOMS/cm^3) / (ATOMS/cm^2)

Layer 2  Layer 3  Layer 4

0 A - Target Depth - 2.5 mm
Depth Profiling - Simulations

ION RANGES

- Ion Range: 2.37 mm
- Straggle: 198. um
- Skewness: -4.8819
- Kurtosis: 38.3065

Levels:
- Layer 2
- Layer 3
- Layer 4

Target Depth: 2.5 mm
Depth Profiling

Hillier et al Microchemical (2016)
Depth Profiling

μ⁻

Ag 1000 μm
Cu 500 μm
Zn 500 μm
Fe 500 μm

Hillier et al Microchemical (2016)
Stopping range is momentum and density dependent

Max available is \(~8.5\, \text{g/cm}^2\)

In Cu \(~1\, \text{cm}\)
In Ag \(~0.8\, \text{cm}\)
In Fe \(~1.1\, \text{cm}\),
In C \(~3.8\, \text{cm}\)
and \(~8.5\, \text{cm} \text{ in Water}\)
Abstract

This report describes the preparation, homogeneity and stability studies, and the subsequent certification of bronze alloys representative of ancient bronze compositions for their As, Pb, Sn, Zn mass fraction. The reference materials (BCR 691) are available as a set of five polished discs diameter 35 mm, thickness 2 mm. The certified mass fractions together with uncertainties are given in the table below. The associated uncertainties are calculated from the combined uncertainties \( u \) multiplied by a coverage factor \( (k = 2) \) (see report).

Certified values and uncertainties \( (k_u) \) for BCR 691 in g.kg\(^{-1}\)

<table>
<thead>
<tr>
<th>Element</th>
<th>Certified composition (%)</th>
<th>Ratio of peak intensity to Cu (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>1.94 ± 0.10</td>
<td>0.5 ± 0.3</td>
</tr>
<tr>
<td>Pb</td>
<td>79 ± 7</td>
<td>n.c.</td>
</tr>
<tr>
<td>Sn</td>
<td>71.6 ± 2.1</td>
<td>7.5 ± 0.5</td>
</tr>
<tr>
<td>Zn</td>
<td>60.2 ± 2.2</td>
<td>6.1 ± 0.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Element</th>
<th>Certified composition (%)</th>
<th>Ratio of peak intensity to Cu (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>0.194 ± 0.1</td>
<td>4.60 ± 0.27</td>
</tr>
<tr>
<td>Pb</td>
<td>7.9 ± 0.7</td>
<td>0.175 ± 0.014</td>
</tr>
<tr>
<td>Sn</td>
<td>7.16 ± 0.21</td>
<td>0.202 ± 0.029</td>
</tr>
<tr>
<td>Zn</td>
<td>6.02 ± 0.22</td>
<td>0.055 ± 0.005</td>
</tr>
</tbody>
</table>

Disclaimer

Whenever, in this report, a commercial product is identified by the manufacturer’s name or label, such identification should in no instance be taken as an endorsement by the Commission or as an indication that the particular product or equipment is necessarily the best available for the particular purpose.

Hillier et al Microchemical (2016)
Example 1: Cultural Heritage

Julia Domna – 3rd Century - CE 211 to 217
Section through a silver-copper alloy Roman denarius, showing the difference in silver fineness between the deliberately-enriched zone near the surface.
Clear evidence of surface enrichment

Probed non-destructively

Hampshire et al, Heritage 2019
Depth Profile

Clear evidence of surface enrichment

Probed non-destructively

Hampshire et al, Heritage 2019
Example 2: Cultural heritage to engineering

Engineering possibilities

- Sword C
- Sword B
- Pure Fe
- Carbon
HYDROGEN STORAGE: $\text{LiNH}_2 + \text{LiH} \leftrightarrow \text{Li}_2\text{NH} + \text{H}_2$

Synchrotron X-ray powder diffraction shows hydrogen release occurs via range of intermediate stoichiometry values – key to easily reversible hydrogen storage.

AMMONIA CRACKING: $2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2$ using $\text{Li}_2\text{NH}$

Variation in lattice parameter of $\text{Li}_2\text{ND}$ on exposure to $\text{ND}_3$ indicates non-stoichiometry during ammonia decomposition reaction – active form of the catalyst is non-stoichiometric.

Example 3: Lithium amide imide ($\text{LiNH}_2 - \text{Li}_2\text{NH}$)
Quantifying the stoichiometry is difficult. By diffraction the scattering (both X-ray and neutron) is dominated by the nitrogen.

QUANTIFYING STOICHIOMETRY WITH NEGATIVE MUONS

Synthesised a series of lithium amide-imide samples with varying stoichiometry:

\[ x\text{Li}_3\text{N} + (2-x)\text{LiNH}_2 \rightarrow 2\text{Li}_{1+x}\text{NH}_{2-x} \]
Different Structure in surface and bulk:

Relaxors display different properties in the bulk and surface – strain (neutrons) and x-rays (32 keV/surface and 67 keV/bulk)
Chemical Homogeneity near surface?

Raman scattering study of the soft mode in Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$

Hiroki Taniguchi, Mitsuru Itoh and Desheng Fu

Raman suggestive of gradient between Mg and Nb near crystal surface (angular dependence)

Negative Muons find no different between Mg and Nb from 100 – 300 microns, but below 100 microns a change in intensity is observed.

Brown et al, JPCM: 2018
Real Space Imaging

A HEXITEC detector module with 1mm thick CdTe mounted on the ASIC and mechanical block.

80 x 80 pixel 250 um pitch

The spectrum from all pixels combined from a 10.5 hour exposure of the Al, C and Fe$_2$O$_3$ sample.
The spectrum from an area of 20x20 pixels next to the C, Al and Fe$_2$O$_3$.

66 keV

75 keV

130 keV

Hillier et al, JPS Conf. Proc. 21, 011042
Isotope analysis

- Different Kα Energy
- Ratio of Intensity relates to isotope abundance

Conclusions

- Elemental analysis is possible using negative muons
- Non destructive
- Depth can be easily controlled
- Can measure deep inside a sample
- Sensitive to all elements
- Imaging is possible
- Ideas?