Application Note: 30006

Fast Scanning Sector Field ICP-MS with Laser Ablation for the Multi-Element Analysis of Elephant Tusk

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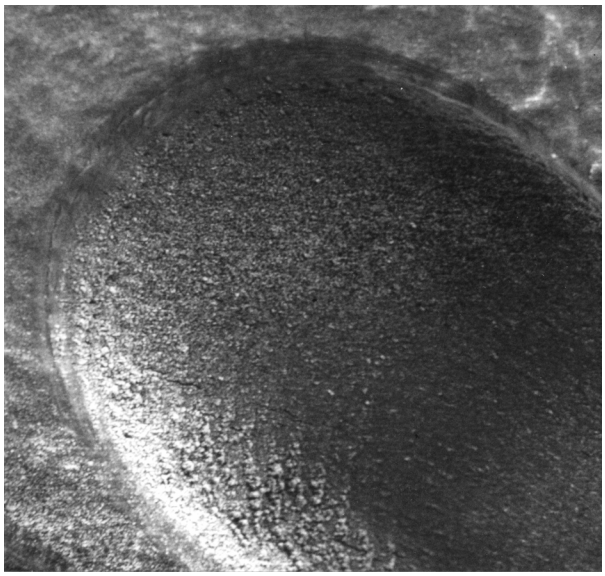
Key Words

- ELEMENT 2
- High Resolution ICP-MS
- Laser Ablation



SEM photo of the ablated track across an elephant tusk sample.

Ivory Trade

1989:

- After ~700,000 elephants were slaughtered for their ivory in the previous decade, the 7th Conference of the Parties to CITES (Convention on International Trade in Endangered Species) approved a worldwide ivory ban

  - *Ivory price fell from $300/kg to $20/kg*

1997:

- One-off 'experimental' trade (50,000kg) allowed

  - *Growing elephant populations*
  - *Lack of significant poaching*
  - *Elephant management policies*

Ivory Trade - Present Situation

1997-2002:

- Increased poaching activities and trade in ivory and ivory fabricated goods
- Ivory price: $250/kg

November 2002: next CITES meeting

- Definition of control & monitoring procedure?
- Relaxation of trade restrictions leading to increased demand…?

Aim of Study

- Are trace element concentrations in elephant ivory representative of ecological regions?

  -Ivory (elephant tusk dentin) contains a Ca deficient hydroxyapatite
  -Other trace elements are incorporated into the dentin
  -Previous work on similar calcified hard biological tissues (fish otoliths etc) have shown this is to be valid

- Assess use of trace metal content as a possible tracer to sources of illegal ivory.

Why Laser Ablation ICP-MS?

- Only small samples required
- Direct sampling
- High sensitivity
- Reduced sample contamination as opposed to sample digestion and subsequent solution based analysis
- Reduced spectroscopic interferences compared to solution based ICP-MS?

Laser Ablation ICP-MS System Used

ICP-MS:
Thermo Scientific ELEMENT 2
Single-collector, magnetic sector

Laser Ablation:
New Wave Research
UP213AI 213 nm
Nd:YAG

Laser Ablation of Elephant Tusk

Fitness for purpose:

- Is a high resolution ICP-MS really necessary?

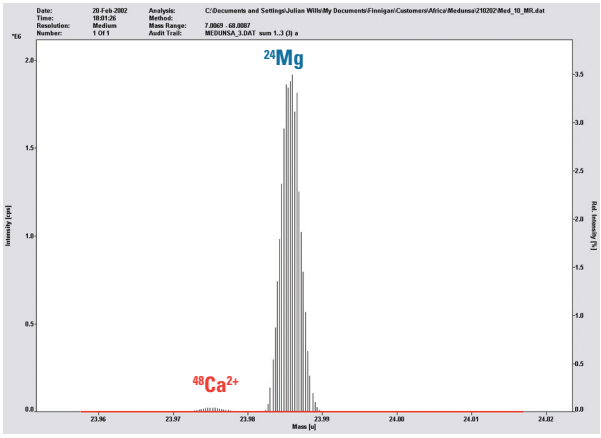
  - *Look for interferences*

Thermo SCIENTIFIC

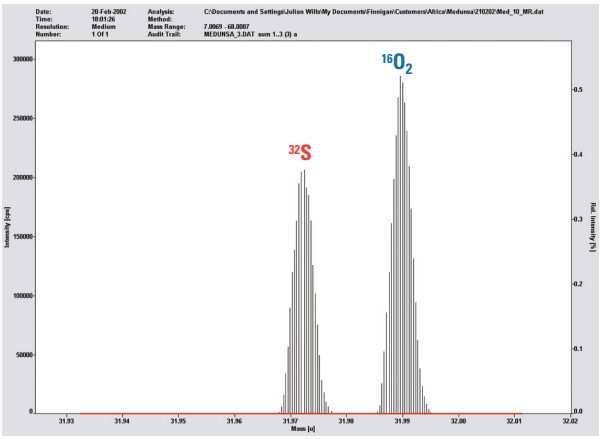
Sample Matrix

Dentin is the ivory forming mass of the tusk:

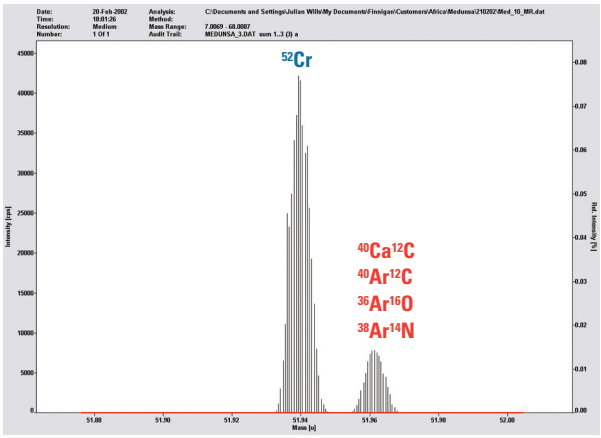
- 20% organic (mostly collagen)
- 80% inorganic
  - *Mainly calcium hydroxyapatite* $(Ca_{10}(PO_4)_6(OH)_2)$
  - *Some* $CaCO_3$, CaF_2 *and* $Mg_3(PO_4)_2$
- ~40% Ca



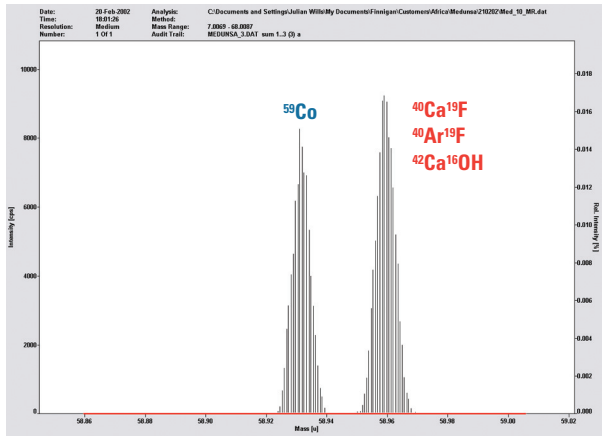
Tusk Interferences ^{24}Mg.



Tusk Interferences ^{32}S.



Tusk Interferences ^{52}Cr.



Tusk Interferences ^{59}Co.

Example:

Laser Ablation of Elephant Tusk

Fitness for purpose:

- High resolution is necessary.
  - *Interferences exist in laser ablation ICP-MS*
  - *Complicated natural matrices lead to complicated ICP-MS spectra*
  - *Only removal of interferences by a difference in mass can guarantee interference free analysis – independent of matrix type*
- Is sector field ICP-MS fast enough?

Reference

Enhanced sensitivity in inductively coupled plasma sector field mass spectrometry for direct solid analysis using laser ablation (LA-ICP-SFMS)

JAAS FULL PAPER www.rsc.org/jaas

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Quote from Conclusion:

The analysis using 35 isotopes showed that the scan speed of the magnet can no longer be considered the limiting factor in quantitative multielement analysis on transient signals when using sector field instruments equipped with fast scanning technology in combination with laser systems.

J. Anal. At. Spectrom., 2002, **17**, 10

Scan Parameters Used:

- Medium resolution (R=4000)
  - *Visible, guaranteed freedom from interferences*
- 27 isotopes measured
  - ^{7}Li - ^{238}U
- Time / sweep: 7.3 s
  - *Analysis time / sweep: 6.6 s*
  - *Delay (magnet and electrical settling time): 0.7 s*
  - *9 sweeps in 66 s*
- Duty Cycle: 90%

Example:

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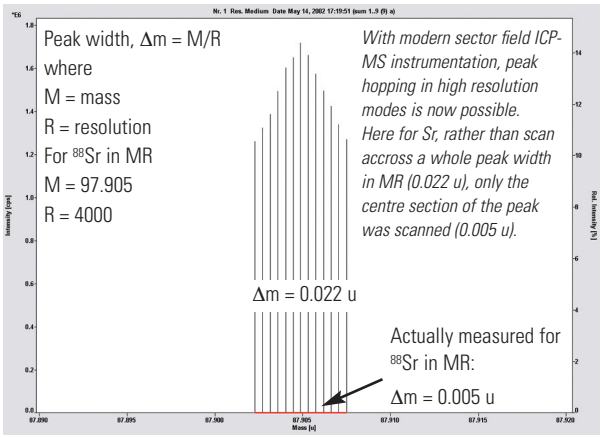
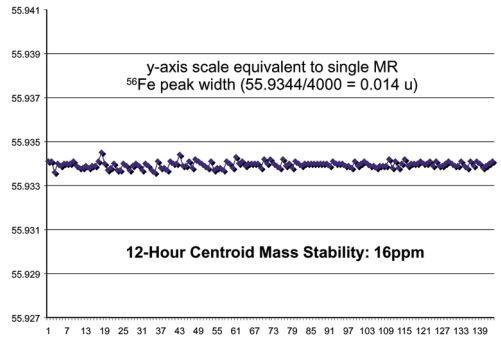
- High resolution is necessary
  - *Interferences exist in laser ablation ICP-MS*
  - *Complicated natural matrices lead to complicated ICP-MS spectra*
  - *Only removal of interferences by a difference in mass can guarantee interference free analysis – independent of matrix type*
- Sector field ICP-MS is fast enough
  - New magnet technology more than doubles scan speed (Thermo Fisher Scientific Application Note AN30011_E)
- Is the mass calibration accurate & stable?



Is the mass calibration accurate & stable?



Twelve Hour ^{56}Fe (MR) Mass Stability.

Example:

Laser Ablation of Elephant Tusk

Fitness for purpose:

- High resolution is necessary
  - *Interferences exist in laser ablation ICP-MS*
  - *Complicated natural matrices lead to complicated ICP-MS spectra*
  - *Only removal of interferences by a difference in mass can guarantee interference free analysis – independent of matrix type*
- Sector field ICP-MS is fast enough for laser analysis
  - *New magnet technology more than doubles scan speed (Thermo Fisher Scientific Application Note AN30011_E)*
- Mass calibrations are accurate & stable
  - Peak jumping now possible in high resolution

System Configuration

New Wave UP213 AI (Aperture Imaged):

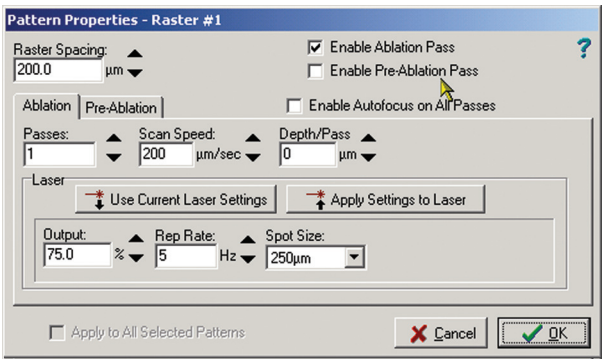
- He as laser cell gas (0.7 L/min)
- Mixed with Ar (0.7 L/min) before plasma torch
- No spray chamber to aid mixing

Thermo Scientific ELEMENT 2:

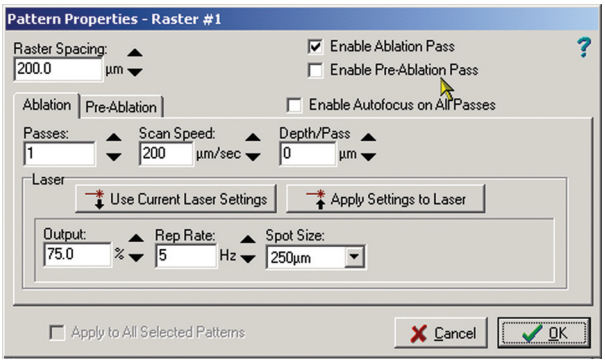
- Al sampler & skimmer cones
- Fast magnet (magnetic scan speed m/z 7 – 240 – 7 < 150 ms)
- 200,000 cps/ppm Th in NIST glass (100 µm spot)
- ThO/Th ratio: 0.1%

Measurement Strategy

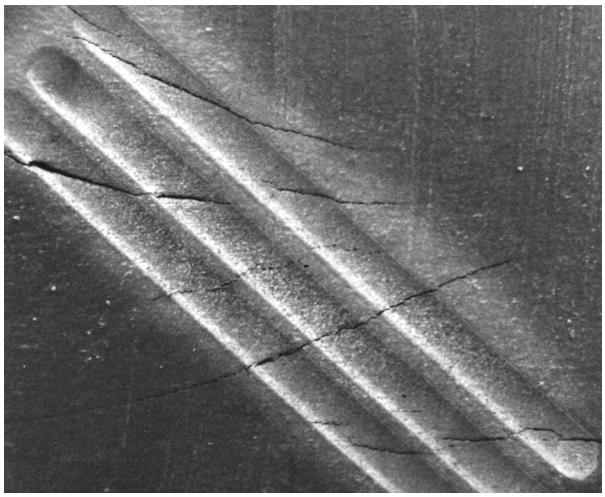
- All analyses made in Medium Resolution (R=4000)
  - Freedom from Ar based interferences (ArO etc)
  - Freedom from matrix induced interferences (CaO etc)
- Quantification
  - NIST glass standards (610, 612 & 614) for external calibration
  - Blank subtraction using gas blank
  - ^{44}Ca as internal standard



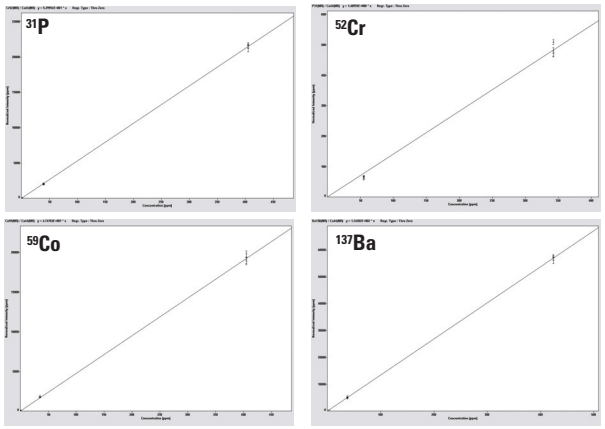
UP213 Pre-ablation parameters: Sample surface initially cleaned (pre-ablation) using these laser parameters (raster pattern).



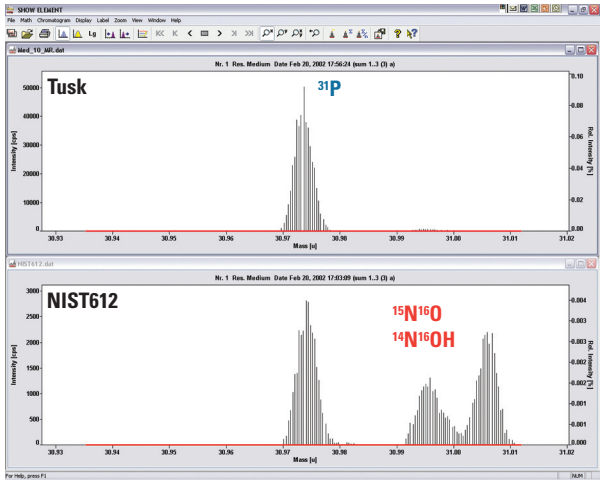
UP213 Analysis parameters: Three measurements made at different sites using these laser parameters (line pattern).



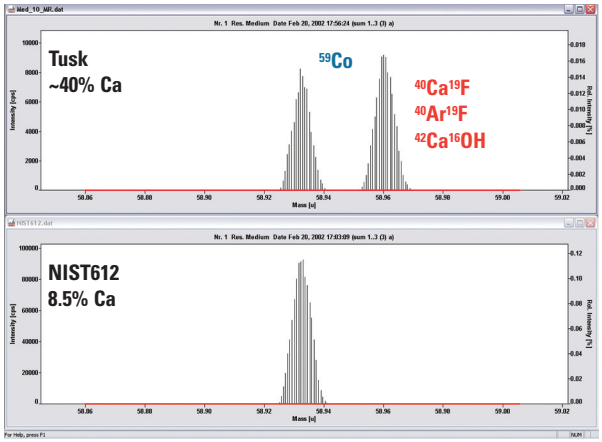
Three line patterns on the cleaned tusk surface.



NIST Glass Calibration Lines.



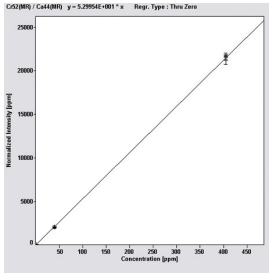
31P: Comparison of interferences.



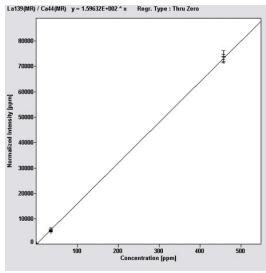
59Co: Comparison of interferences.

Results

	52Cr(MR)
LoD (ppm)	0.02
Site 1 (ppm)	0.37
Site 2 (ppm)	0.37
Site 3 (ppm)	0.39
Average (ppm)	0.38
%RSD	3.5



	139La(MR)
LoD (ppm)	0.002
Site 1 (ppm)	0.038
Site 2 (ppm)	0.039
Site 3 (ppm)	0.042
Average (ppm)	0.040
%RSD	5.2



Conclusions

High resolution sector-field ICP-MS is an ideal elemental detector for laser ablation analyses in complex environmental samples:

- Only high mass resolution can guarantee interference free multi-elemental analysis - independent of the sample matrix - with a single set of analysis parameters.
- Historical concerns of: *Scan speed, mass accuracy and mass stability* are no longer an issue with current instrumentation.
- Sector field ICP-MS provides improved detection limits due to a better signal to noise ratio and interference-free analysis.
- Due to the higher sensitivity, lower laser energies can be used and smaller samples analysed.

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