

# LA-ICP-MS and IRMS investigations on packaging and duct tapes

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Shirly Montero, Wim Wiarda, Peter de Joode,  
Gerard van der Peijl

Nederlands Forensic Institute (NFI)



## Contents

- **Introduction**
- Applications
  - Packaging tapes - (LA) ICPMS/IRMS
  - Duct tapes - LA ICPMS/IRMS
- Conclusions



## Intro - Use of elements and isotopes?

- Elemental composition
  - XRF, ICP AES,...
  - trace elements (ppt-ppm)
- Isotopic composition
  - variation of isotopic ratios is used for extra information
  - extra dimension relative to elemental composition
    - differentiation of pure chemical compounds
- New Analytical Techniques:  
**ICPMS and IRMS**



## Inductively Coupled Plasma Mass Spectrometry (ICPMS)

### What is it?

—Chemical compounds are introduced into a hot torch (8000 K) and broken down to ions that are analysed in a dedicated MS

—Higher atomic elements (Fe, Mn, Pb, Sr)

### Why is it relevant?

- specific elemental information (Cu, Cr, V)
- multi-element capability (comparisons)
- high sample throughput (capacity)
- extremely sensitive (trace elements)
- isotopic geographical variation (e.g. Pb)
- lateral/depth info for LA-ICPMS



## Isotope Ratio Mass Spectrometry (IRMS)

### What is it?

—Chemical compounds are converted in-line to relevant simple compounds and analysed in a dedicated Sector Field MS

—Lower atomic elements (H, N, C, O, S)

### Why is it relevant?

- high precision of isotope ratios ( $^{13}\text{C}/^{12}\text{C}$ ) major elements (H, C, N, O)
- highly accurate isotopic shifts in combination with reference material ( $\delta^{13}\text{C}$ )
- forensic potential (comparison and geographical sourcing) provided by variations in isotope ratio's through physical, chemical and biological processes



## ICPMS/IRMS applications - potential

- |                         |                        |
|-------------------------|------------------------|
| • paint                 | • bricks, cement, tile |
| • polymers (PE,PP, PVC) | • wall material safes  |
| • rubbers               | • matches              |
| • fibers                | • metals               |
| • ink                   | • paper                |
| • tape                  | • hair                 |
| • glue                  | • bones                |
| • kits                  | • nails                |
| • cosmetics             | • candles              |
| • soaps, detergents     | • (illegal) drugs      |
| • soil                  | • tracers              |
| • glass                 | • ...                  |



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## Packaging tapes



## Brown packaging tape - introduction

Until recently encountered in most of the violent crimes where tape is found

- Three brands brown packaging tapes acquired, different outlets and different times:
  - TESA, V&D and Ruban Embal (Blokker)
- Tape layer structure
  - release coating /backing(PP)/primer/glue (PSA)
  - backing film:
    - bi-axially oriented polypropylene (BOPP)
  - glue-Pressure Sensitive Adhesive (PSA): 20-50 g/m<sup>2</sup>



## Tapes - techniques

- 'Classical' techniques
  - visual/microscopic (colour, thickness, width, appearance)
  - FT-IR (backing and glue typing)
  - XRF (major and minor elements in glue)
- New Techniques
  - ICPMS
  - LA ICPMS
  - IRMS
- Conclusions packaging tapes



## Tape - results 'classical' techniques

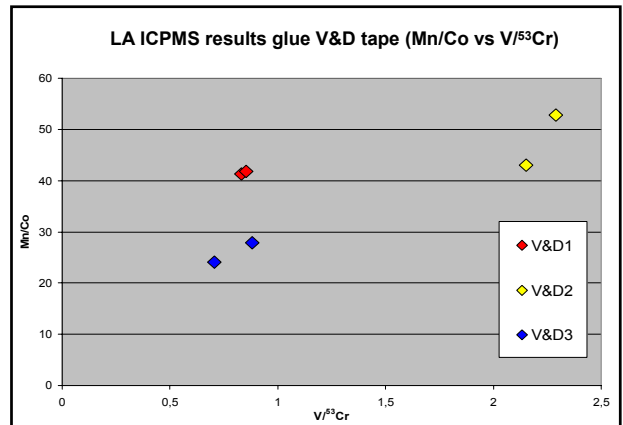
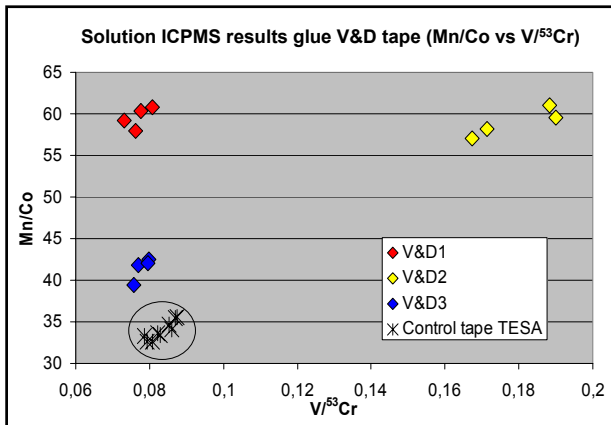
- Glue
  - acrylic (Tesa and V&D) or
  - rubber type (Ruban Embal)
- Backing
  - PP for all 3 brands
- Brands can be discriminated
- Partial discrimination samples from one brand



## Tape - ICPMS - experimental

- Glue layer is investigated
  - no variation of trace elements in backing layer
- Finnigan Element HR-ICPMS system
  - LR/MR/HR
  - M/ΔM=3000 (MR) is used
- Solution ICPMS - Sample preparation
  - microwave digestion glue layer (closed quartz vessel, HNO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> mixture, 32 mins irradiation)
  - V, <sup>52</sup>Cr, <sup>53</sup>Cr, Co, Mn, Ni, Cu, Zn can be used
- Laser Ablation ICPMS
  - 266 nm Nd YAG laser, 2 mJ, spot 80 μm, 10 Hz, 60 s, 1 mm<sup>2</sup>





**Tape - IRMS - experimental**

Europa Scientific Geo 20-20 instrument

- Full tape, glue layer and backing layer
- EA-IRMS (Elemental Analyzer IRMS)
- <sup>2</sup>H/<sup>1</sup>H, <sup>13</sup>C/<sup>12</sup>C and <sup>18</sup>O/<sup>16</sup>O (O only in glue 2 types)
- <sup>2</sup>H/<sup>1</sup>H, <sup>13</sup>C/<sup>12</sup>C: 0.5 mg = 5 mm<sup>2</sup> **full tape** sample
- <sup>2</sup>H/<sup>1</sup>H, <sup>13</sup>C/<sup>12</sup>C: 0.5 mg **backing** or 0.5/1.0 mg **glue**
- <sup>2</sup>H/<sup>1</sup>H, <sup>13</sup>C/<sup>12</sup>C and <sup>18</sup>O/<sup>16</sup>O analyses using different conditions

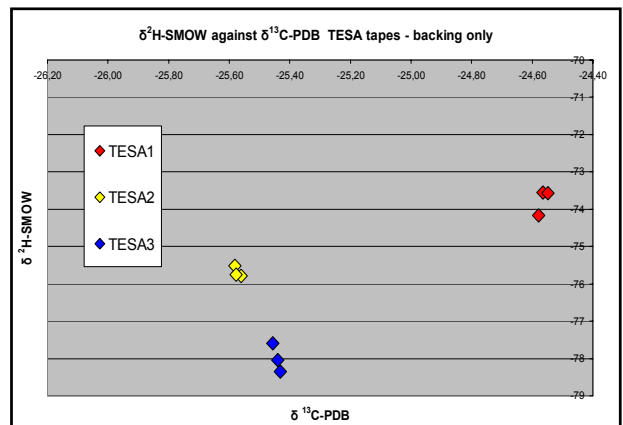
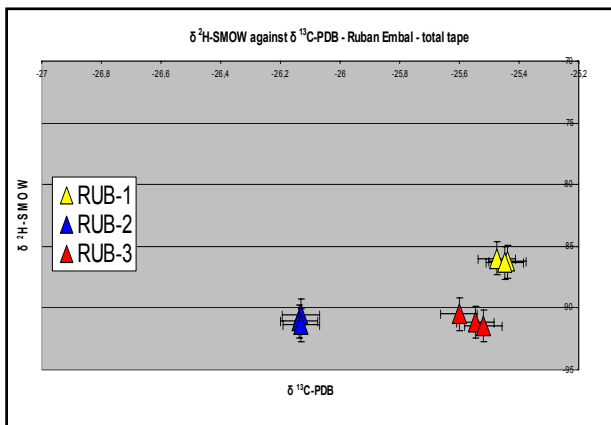
*IRMS services provided by Iso-Analytical Ltd (Sandbach, UK)*

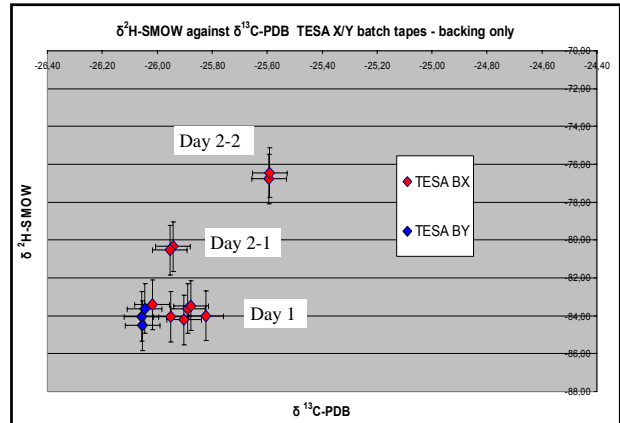
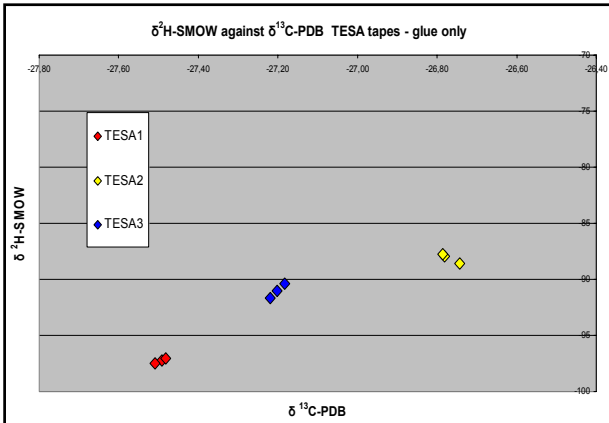
**TAPE - IRMS -  $\delta^{13}\text{C}$  definition**

$$\delta^{13}\text{C} (\text{‰}) = (R_{\text{smpl}}/R_{\text{std}} - 1) \times 1000$$

$R_{\text{smpl}} = ^{13}\text{C}/^{12}\text{C}$  of a sample, and  
 $R_{\text{std}} = ^{13}\text{C}/^{12}\text{C}$  of an international standard (e.g. VPDB)

$\delta$ -notation represents a part-per-thousand difference from a standard



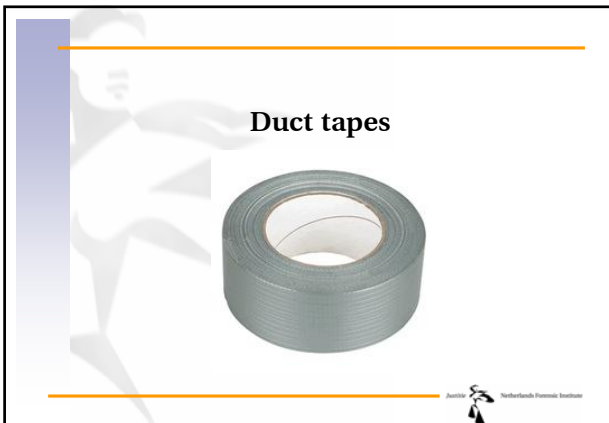


### Packaging tape - conclusion

- Both ICPMS and IRMS excellent results
  - All tape rolls could be discriminated for each brand using  $\delta^{13}\text{C}$  and  $\delta^2\text{H}$  results or trace element info
  - For the two oxygen containing brands, samples could also be discriminated using the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  results
- IRMS - ICPMS
  - ICPMS inherently more sensitive to contamination
  - IRMS focuses on the abundant elements (H, C and O) and is expected to be less sensitive to contamination problems
  - Extremely interesting is discrimination using only clean backing material (no contaminating debris)

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### Duct tape - introduction

Recently more encountered in violent crimes where tape is found - application to casework

Tape layer structure

- release coating / **backing(PE)** / primer / **textile web / glue (PSA)**
- backing film: polyethylene
- **textile web - eg polyester**
- glue-Pressure Sensitive Adhesive (PSA)

## Duct tape - casework/reference

### Casework

armed robbery - victims bound with gray duct tape T1  
tape roll T2 (TESA) thrown out of car suspects

### Reference NFI tapes

40 gray duct tapes collected in the Netherlands /  
8 different brands of duct tapes: Pattex, TESA,  
Gamma, Deltafix, Master, V&D, B1, B2  
12 TESA tapes (11\*TESA Extra Power Universal +  
1\*Extra Power Perfect)



## Duct tape - 'Classical' techniques

- 'Classical' techniques
  - visual/microscopic (colour, thickness, width, appearance)
  - FT-IR (backing and glue typing)
  - XRF (major and minor elements in glue)
- Casework samples T1 and T2 not discriminated



## Duct tape - 'Classical' techniques 2

- Vis +FT-IR:
  - All brands NFI tapes could be discriminated
  - TESA: 5 subgroups characterized (4+3+3+1+1)
  - Casework samples in TESA subgroup with 4 tapes
- XRF
  - Casework samples discriminated from all other NFI tapes
  - TESA discriminated from all other brands
  - 3 TESA tapes (3 Praxis shops, one day) not discriminated - group G1
- TESA Extra Power Universal for LA ICPMS+IRMS*



## TESA EPU duct tape - LA Q ICPMS + IRMS

- LA Q ICPMS (backing+glue):
  - Casework samples discriminated from NFI TESA tape
  - G1 (Praxis) NFI TESA tapes not discriminated
  - Similar discrimination as Vis/FT-IR
- IRMS (backing+glue):
  - <sup>2</sup>H/<sup>1</sup>H and <sup>13</sup>C/<sup>12</sup>C
  - Casework samples discriminated from NFI TESA tape
  - G1 (Praxis) NFI TESA tapes not discriminated + 1 other TESA tape
  - Better discrimination than Vis/FT-IR



## TESA EPU duct tape - Overview results

	Vis/FTIR	XRF	LA ICPMS	IRMS
TESA1	1	1	1	1
TESA2	1	1	1	1
TESA3	2	2	2	2
TESA4	2	8	2	2
TESA5	3	3	3	2
TESA6	4	4	4	3
TESA7	3	5	3	2
TESA8	2	6	2	4
TESA9	2	7	-	2
TESA10	1	1	1	1
TESA11	3	9	3	5



## TESA EPU NFI duct tapes - discussion

- Both casework samples not discriminated
  - Casework samples discriminated from all NFI tapes
- Classical techniques already useful
  - Variation in glue, textile and backing
- XRF best discrimination
  - XRF can often not be used due to contamination
- IRMS good discrimination
  - IRMS glue can often not be used due to contamination
- G1 (Praxis) NFI TESA tapes not discriminated
  - One production batch?



## TESA NFI duct tapes - discussion 2

Always be aware of unifiers!

Orange-brown PE particles (1-2 mm) retrieved from both roll of tape as well as from similar tape encountered at crime scene



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## Conclusions

- ICPMS + IRMS - Strong combination
- Classical techniques already powerful
  - Discrimination between brands
  - Partly further discrimination — especially duct tape
- Extra use of info LA Q ICPMS + IRMS
  - Packaging tape - inter-/intra- batch
  - Duct tape - confirmation Vis/FT-IR/XRF results
  - In practical casework often not IRMS glue
  - For PVC tapes removal of glue also removes additives (plasticisers) from backing materials

## Other actual NFI applications IRMS

- Comparison
  - Charred jerrycan remains from arson residue
  - Electrical cable insulation
  - Sawdust
  - Paper
  - Polypropylene Rope
  - Motor oils (IRMS + GC-IRMS)*
  - Blue jeans (IMRS + LA-IRMS?)*
- Tracing geographic origin and movements of humans

## Literature references ICPMS/IRMS tape NFI

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