Application of spectrochemical profiles for the forensic characterization and identification of electrical tapes.

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Purpose of the study

To design, develop, and evaluate a **chemical searchable database** to:

1. Provide an ***automated*** platform for characterization of materials that underpins the ***interpretation of forensic evidence***.
2. Provide support to forensic and intelligence investigations using ***chemical signatures for classification/connection/association*** of forensic evidence with common source(s).

Challenges of databases

- Reproducible
- Informative
- Searchable
- Relevant
- Updated

Evaluation and validation of the database

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1. Assessment of the forensic utility of each analytical method
   - Discrimination and association (error rates)
   - Blind studies
   - Fundamental information about limitations, advantages and chemical characterization provided by each method and material.

1. Validation of the database searching algorithms
   - References vs. testing database
   - Percent of correct associations
     - PLSDA (top-five similar classes)
     - KNN (top-ten spectra, replicates)
     - Performance compared to spectral overlay (outside of database)

REFERENCE database:

- ***Tapes:*** *912 files from 96 tape rolls*

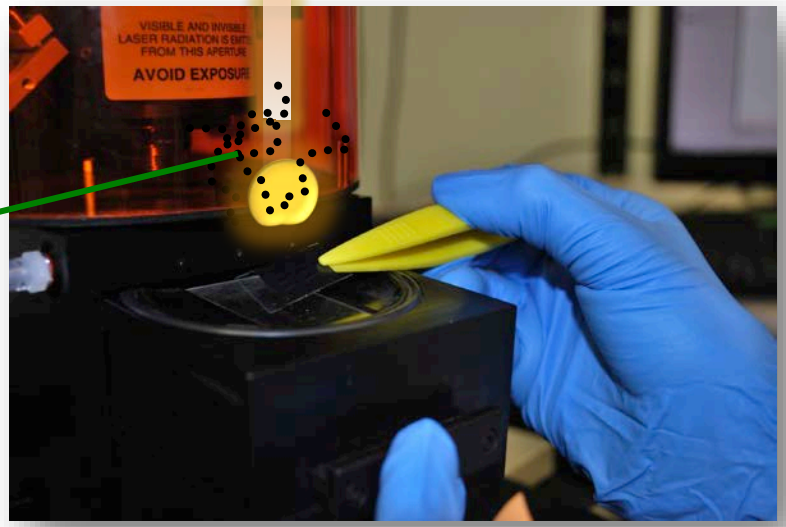
EXPERIMENT / TEST database:

Duplicate controls

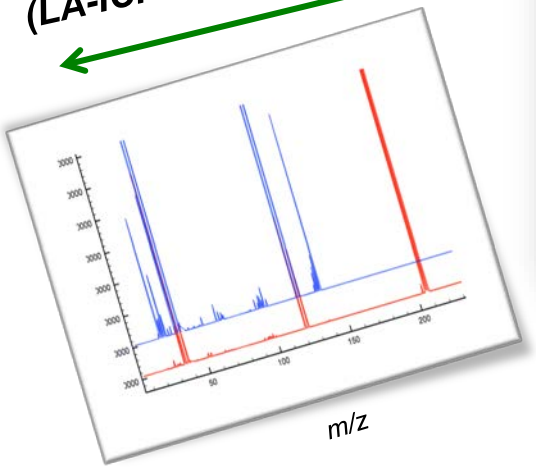
- ***Tapes****: 657 files from 96 tape rolls*

WHY LA-ICP-MS?

- ***Fast, real time** and **direct** solid sampling*
- *High **analytical sensitivity, selectivity***
- ***No sample preparation***



Ablated particles carried to ICP-MS for detection (LA-ICP-MS)



Hypotheses of the study

Inter-roll variations of the elemental composition **is greater than** the **intra-roll variation within a single roll** providing discrimination between sources.

The **elemental composition** of electrical tapes analyzed by LA-ICP-MS provides **enhanced discrimination potential**, **improved characterization capabilities** and **stronger conclusions** than those provided by conventional methods such as SEM-EDS, as a result of their superior sensitivity, selectivity and precision.

- *What is the quality of the elemental signature provided by LA-ICP-MS?*
- *Identification of robust statistical tools for the interpretation of the elemental profiles.*

Description of the collection set

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- **Tape collection set**
  - **96 black electrical tapes**
    - 90 tapes provided by the FBI and already analyzed by traditional methods[*1,2] (40 different product/model, 24 different brands,16 different UL numbers, 4 different countries of origin)
    - 6 tape rolls (3 different brands, 2 different UL numbers, 3 different countries of origin)
    - Each tape analyzed in 6-12 replicates from different sections of the roll

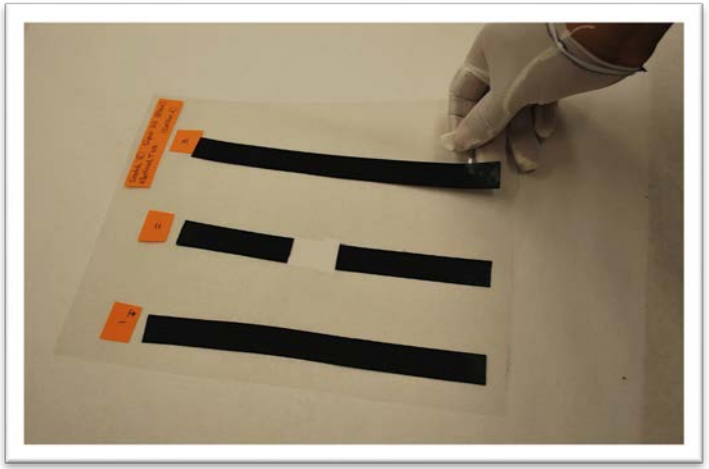
*[1] *Mehltretter AH, Bradley MJ, and Wright DM. Analysis and discrimination of electrical tapes: Part I. Adhesives, Journal of Forensic Sciences, 2011, 56(1): 82-94.*

*[2] *Mehltretter AH, Bradley MJ, and Wright DM. Analysis and discrimination of electrical tapes: Part II. Backings, Journal of Forensic Sciences, JFS, 2011, 56(6); 1493-1504.*

Within roll homogeneity study

- Intra-roll variability
  - Each tape roll was divided into 6 sections.
  - Intra-roll homogeneity: 36 replicates (6 sections, 6 replicates each)

ID #	Brand	Year	Country
T02	Scotch (Super 88+)	2011	USA
T03	Scotch (Super 33+)	2011	USA
T04	Scotch	2007	USA
T05	Commercial Electric	N/A	China
T06	General Electric	2011	Taiwan
T07			



Intra-roll homogeneity results

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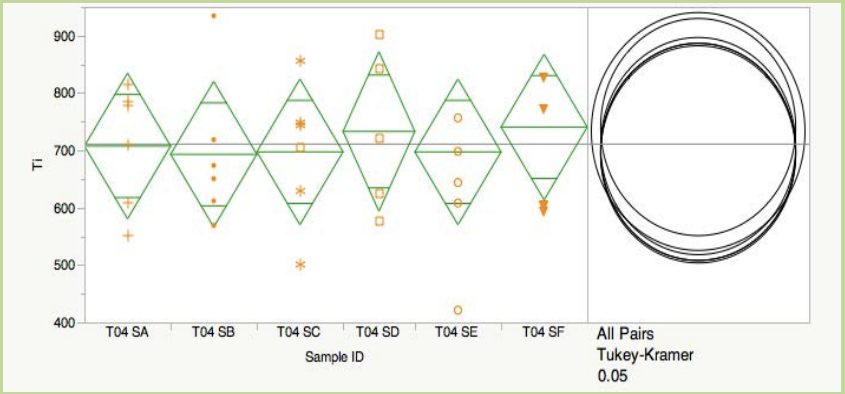
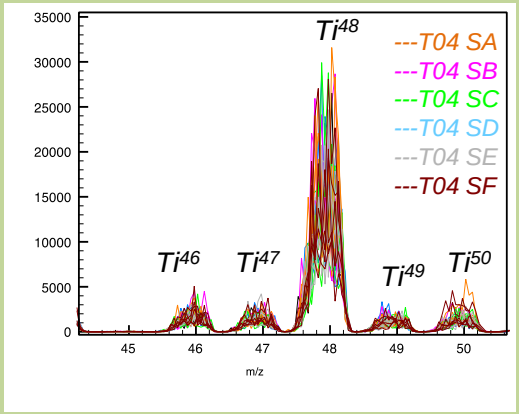
ANOVA- Tukey for Tape T04

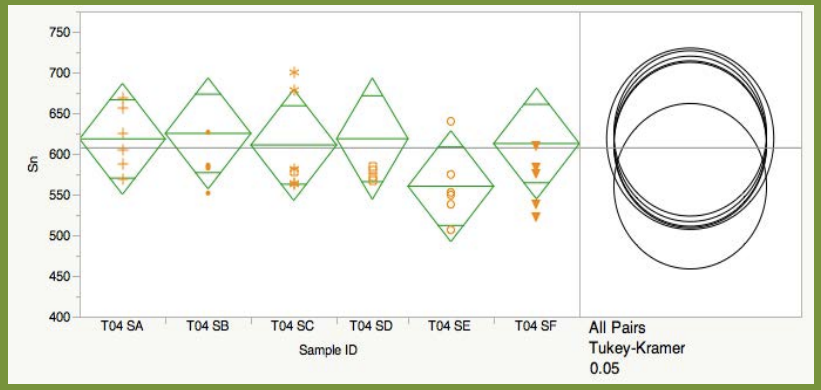
Spectral Overlay Tape T04

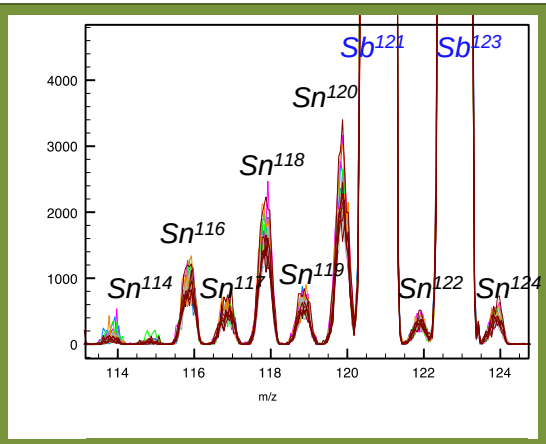
Titanium



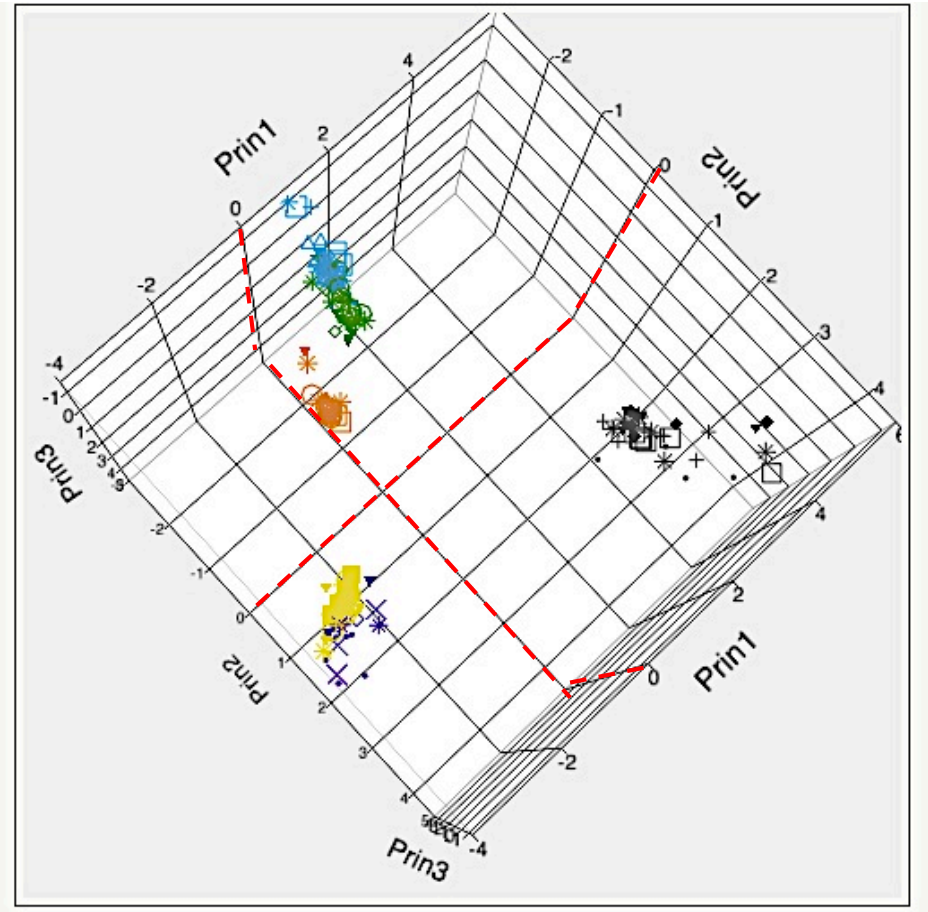


Tin





Inter and Intra-roll variations - PCA



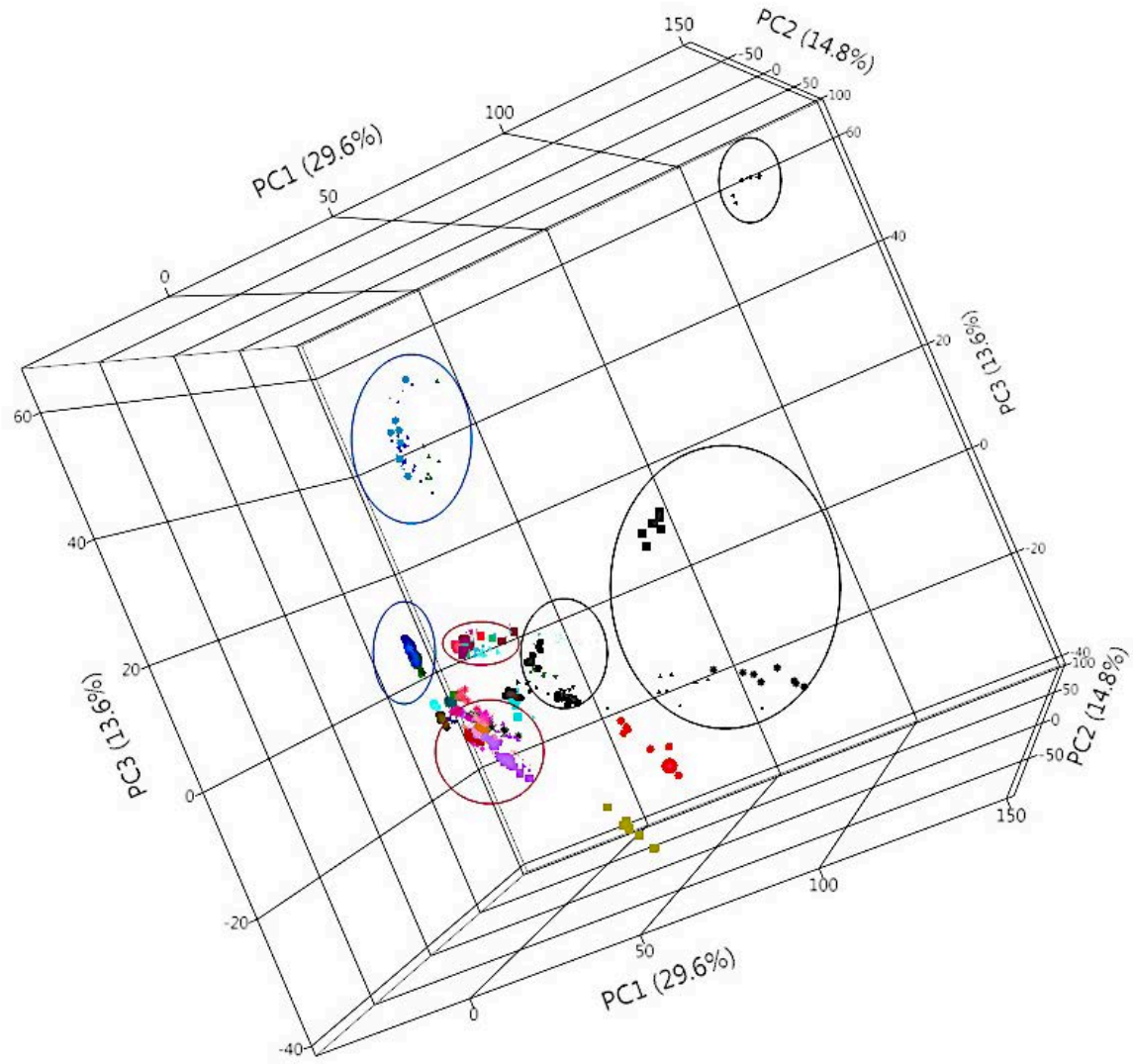
---T02 (Scotch 88+)
---T03 (Scotch 33+)
---T04 (Scotch)
---T05 (CE)
---T06 (General Electric)
---T07 (General Electric)

PC1: 39.8%
PC2: 25.8%
PC3: 17.1%

Intra-roll: *All tape sections within the same roll were grouped correctly*

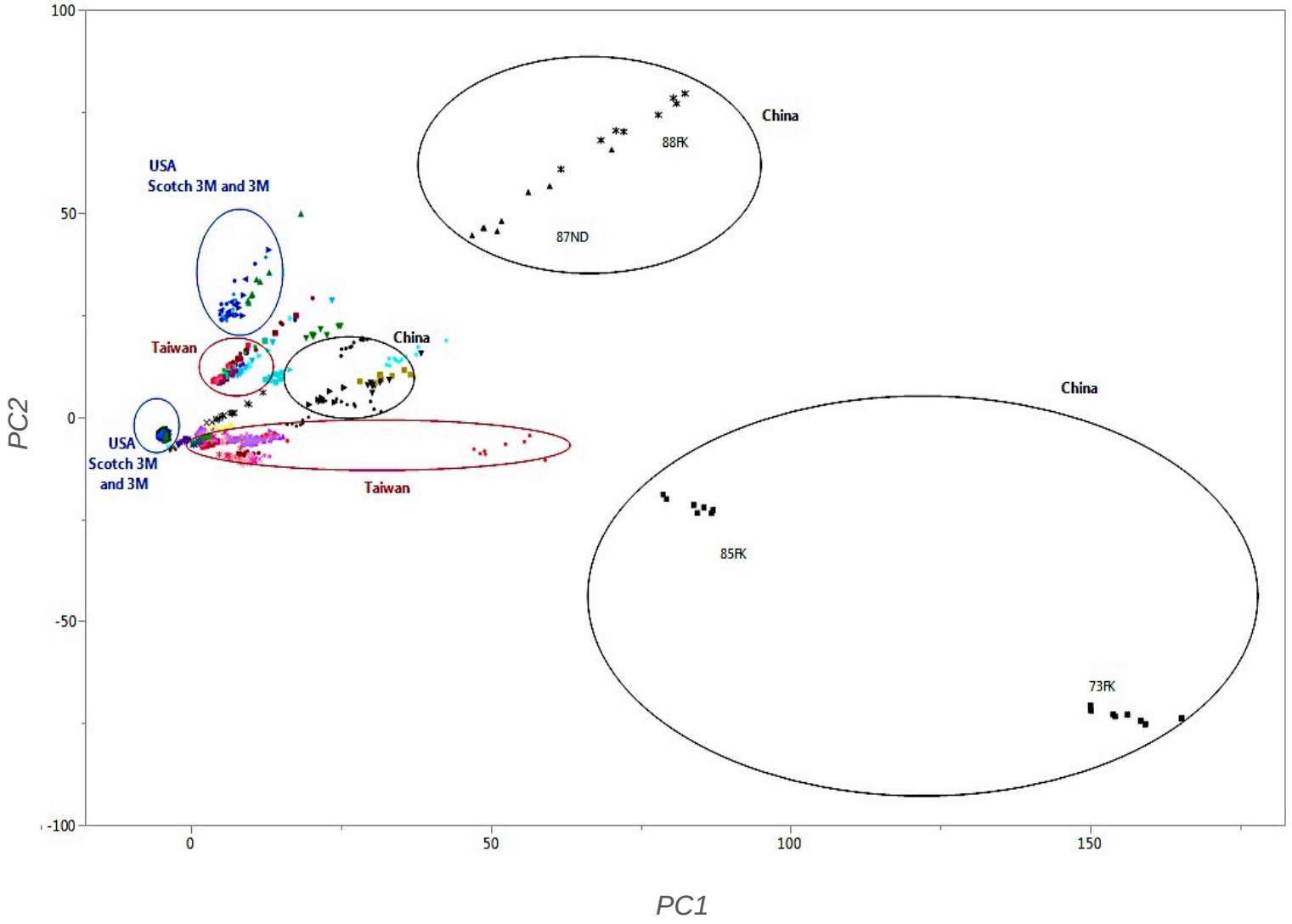
Inter-roll: *All tape rolls were correctly separated, except those of same package (T06,T07) or same brand (UL, year T02, T03)*

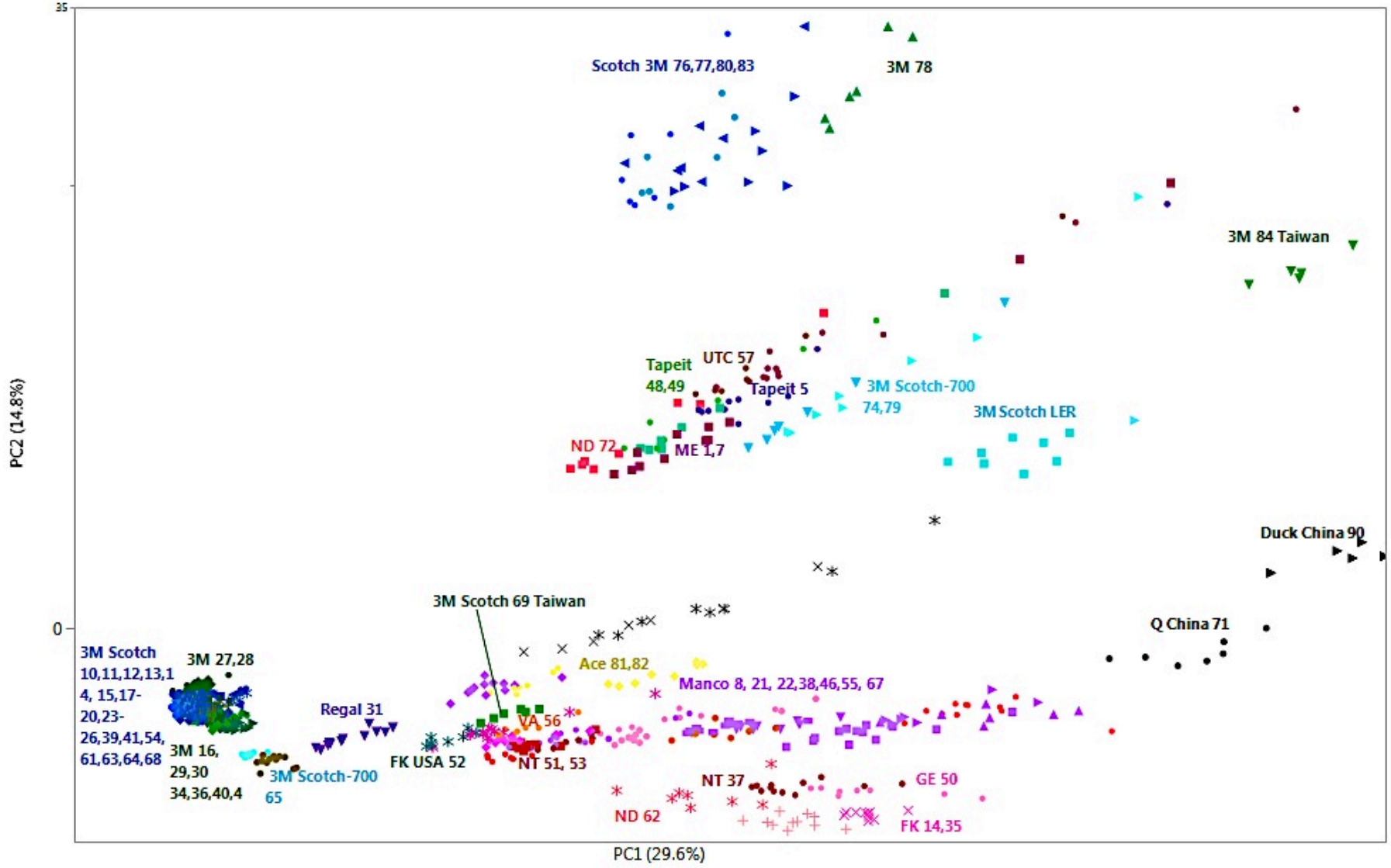
Classification capabilities of LA-ICP-MS: PCA



China --
USA -- --
Taiwan -- -- --
UK--

90 tapes, 4 countries, 24 brands

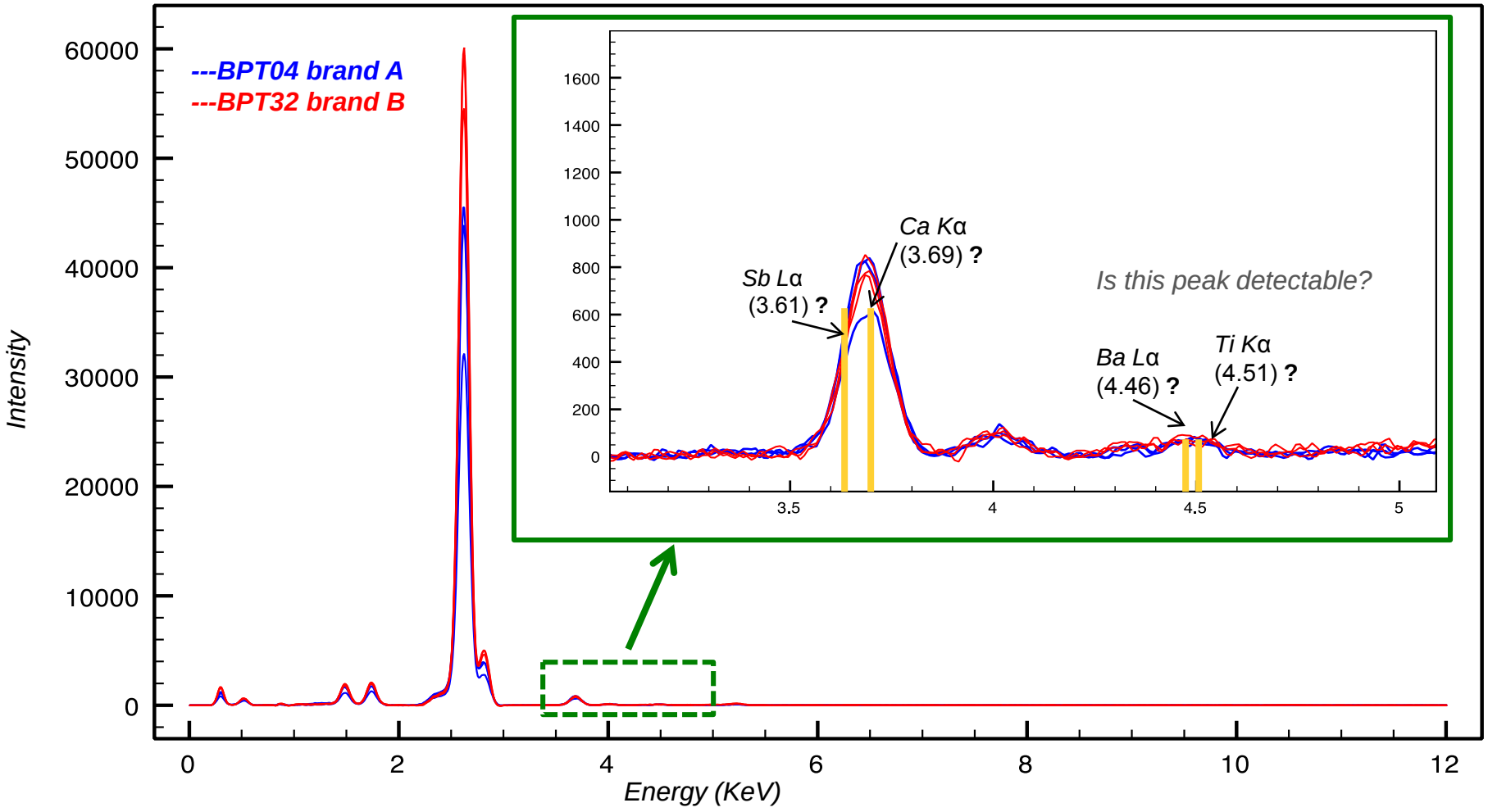

100
50
0
-50
-100
0
50
100
150
PC2
PC1
China
88RK
87ND
USA
Scotch 3M and 3M
Taiwan
China
USA
Scotch 3M
and 3M
Taiwan
China
85RK
73RK


35
0
PC2 (14.8%)
PC1 (29.6%)
Scotch 3M 76,77,80,83
3M 78
3M 84 Taiwan
Tapeit 48,49
UTC 57
Tapeit 5
3M Scotch-700 74,79
3M Scotch LER
ND 72
ME 1,7
Duck China 90
Q China 71
3M Scotch 69 Taiwan
3M Scotch 10,11,12,13,14, 15,17-20,23-26,39,41,54, 61,63,64,68
3M 27,28
Ace 81,82
Manco 8, 21, 22,38,46,55, 67
Regal 31
VA 56
3M 16, 29,30 34,36,40,4
3M Scotch-700 65
FK USA 52
NT 51, 53
NT 37
GE 50
ND 62
FK 14,35

Inter-roll variations of the elemental composition **is greater than** the **intra-roll variation within a single roll** providing discrimination between sources.

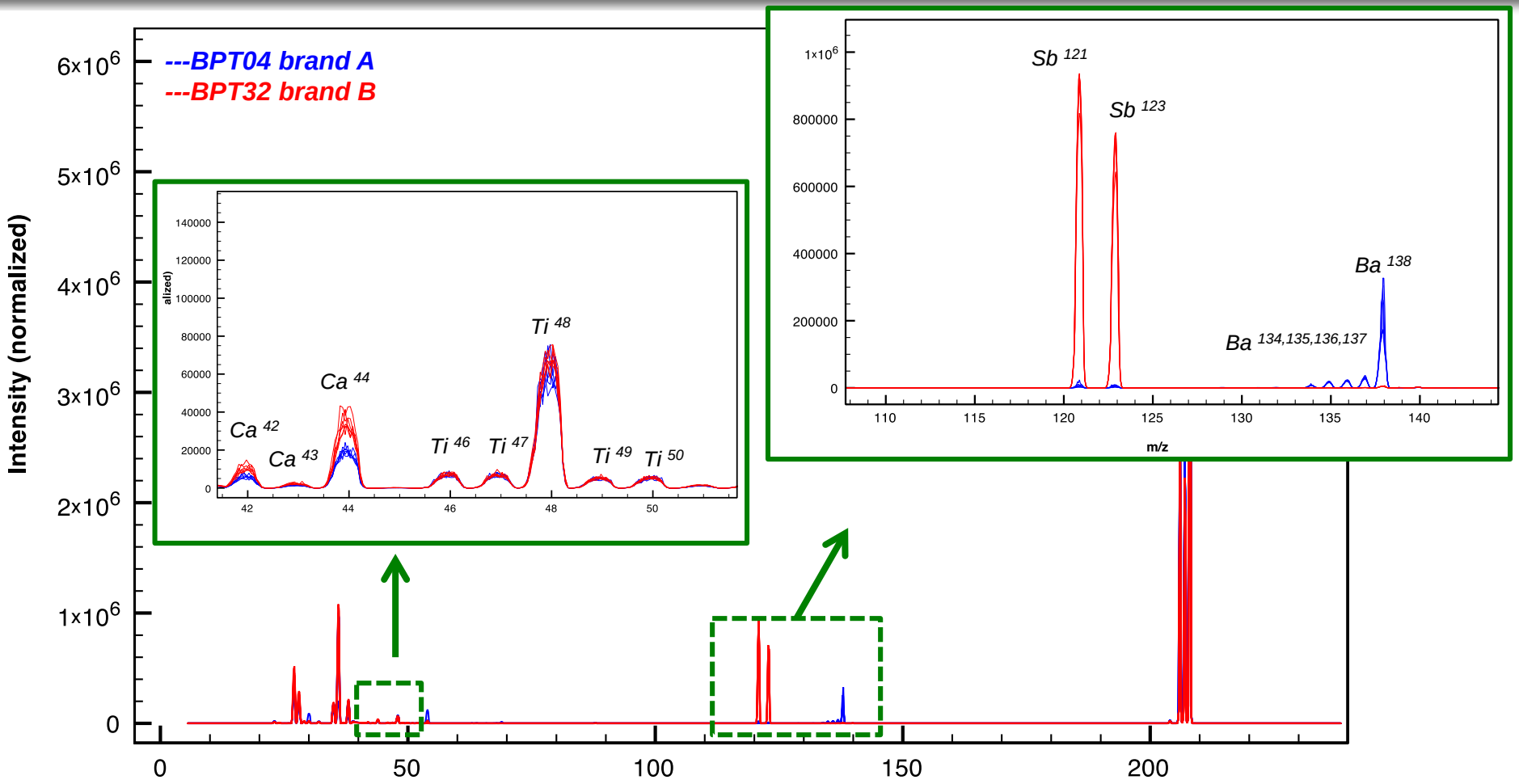
LA-ICP-MS elemental signatures provide classification at the manufacturing level.

Elemental analysis of tape by SEM-EDS: current limitations



SEM-EDS Spectra of backings of two black electrical tapes (different brands, BPT04 and BPT32)

Elemental analysis by LA-ICP-MS: improved sensitivity, selectivity, discrimination and confirmation.



LA-ICP-MS spectra of backings of two black electrical tapes (different brands, BPT04 and BPT32)

Evaluation of the discrimination potential

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	SEM-EDS	LA-ICP-MS
# samples from different sources	90 (4005 pairs)	90 (4005 pairs)
Percent discrimination	**87.3 %** (3496 out of 4005)	**93.9 %** (3760 out of 4005)
Percent of indistinguishable pairs (false inclusions)	**12.7%** (508 out of 4005)	**6.1%** (245 out of 4005)
# of distinct "groups"	15	50

# of pairs = n(n-1)/2
n= number of tapes from different sources

Elemental profiles for characterization

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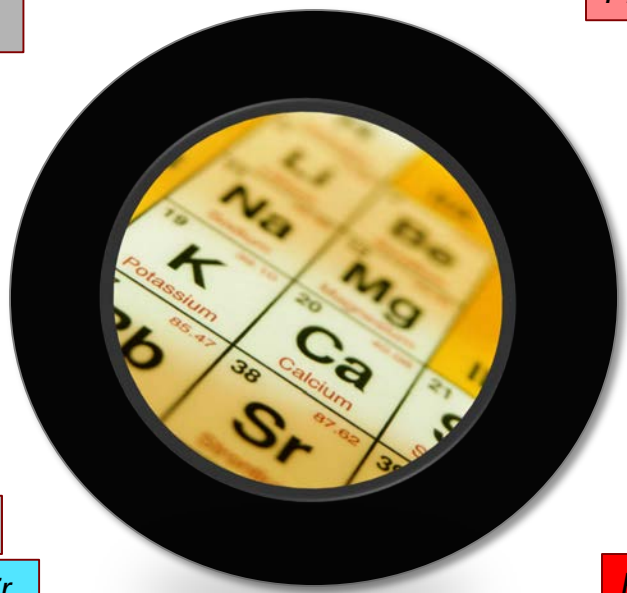


Additives/ Heat resistance
Na, Mg, Ca, Cr, Sr, Zr, Nb, Sn

Polymer catalyst, precursors:
Li, B

Fillers:
Na, Ca, Al, Si, Ba, S, Ti, Fe, Zn, Cd, Pb

Coatings
Al, P, Ca, Si
Stabilizers
Si, Ca, Pb

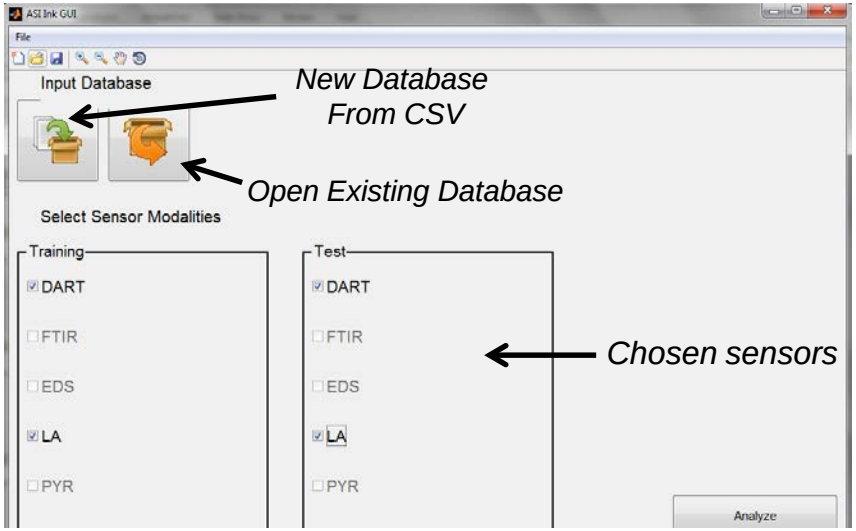
Metallic driers
Cu, Zr, Sr, Mn, Pb, Zn, Zr, Bi, Ba

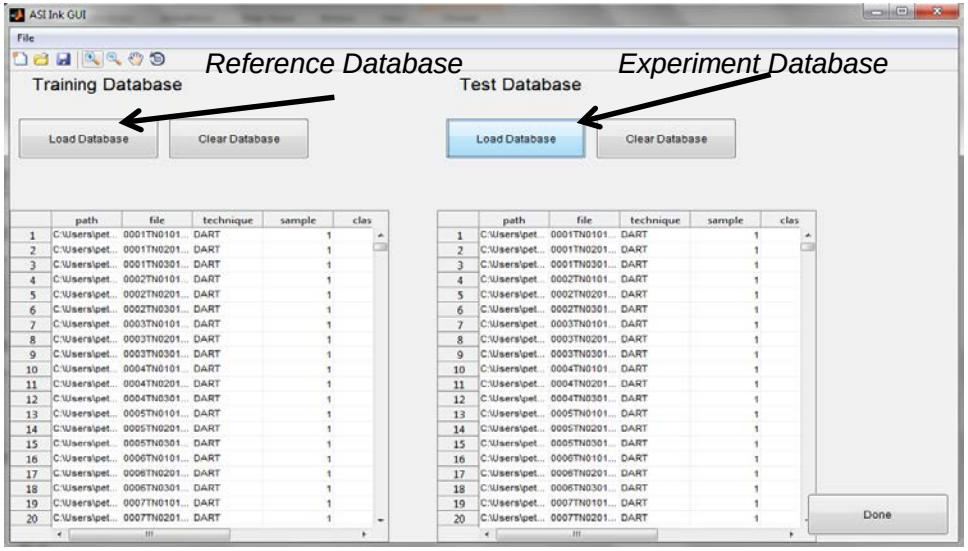
Thinner/diluent of metallic driers
Fe, Zn, Pb

PVC polymer
Cl

Flame Retardants
Br, Mo, Sb

Database


ASI Ink GUI
File
Input Database
New Database From CSV
Open Existing Database
Select Sensor Modalities
Training
DART
FTIR
EDS
LA
PYR
Test
DART
FTIR
EDS
LA
PYR
Chosen sensors
Analyze


ASI Ink GUI
File
Reference Database
Experiment Database
Training Database
Test Database
Load Database
Clear Database
Load Database
Clear Database
path
file
technique
sample
clas
Done

Example of unknown control correctly associated with Tape 73

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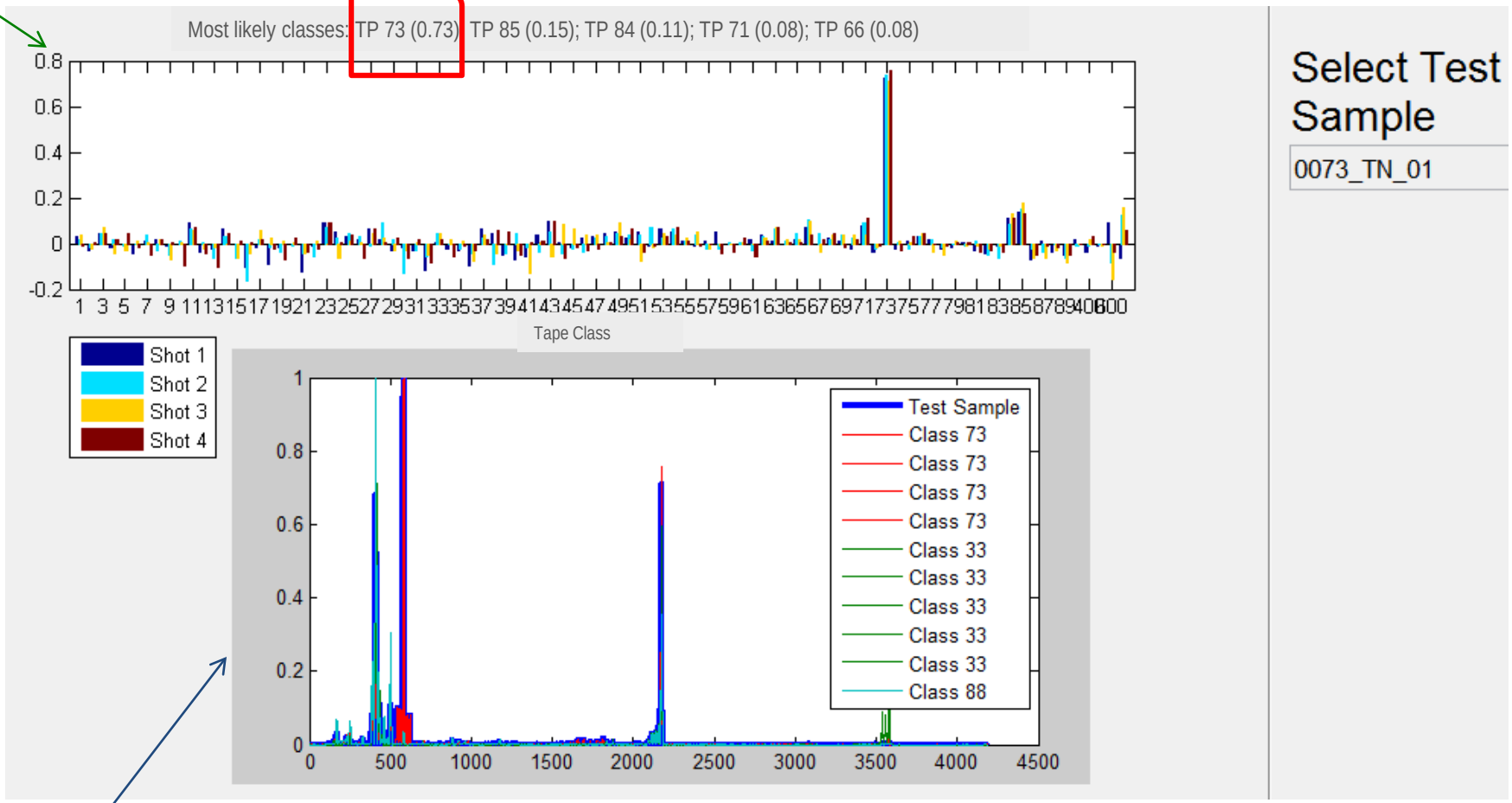
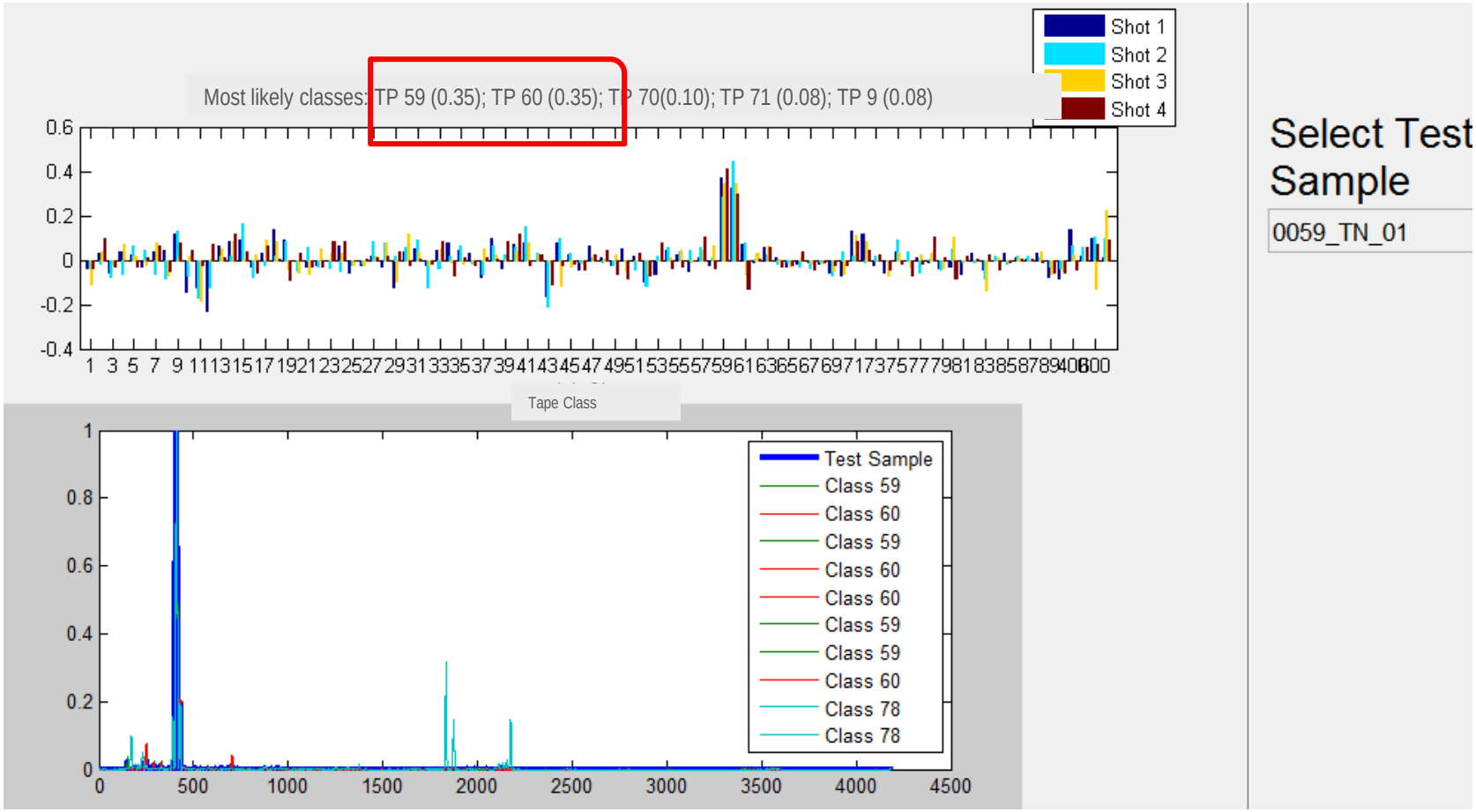
PLSDA classification: Top 5 most similar in the reference database



KNN spectral comparison: Top 10 most similar spectra (replicate spectra)

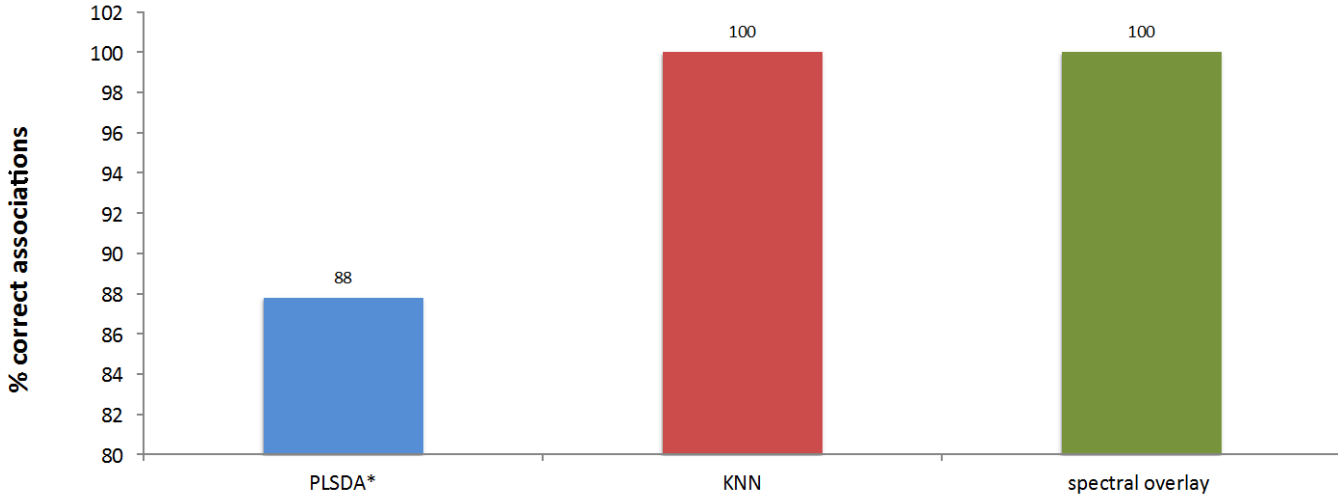
Example of correct association and correct “grouping”



Both Tape 59 and 60 are Tuff ™ Hand Tools from China
Tape 59 and 60 are not distinguished by LA-ICP-MS or by any of the current methods

Evaluation of Correct Associations/Classifications –Blind Duplicate controls

- 129 duplicate controls (from 94 different tapes)
  - **90 Blind duplicate** controls for all 90 electrical tapes
  - **39 Intra-day and inter-day blind duplicate controls** (4 tapes, analyzed up to 2 months apart)
- LA-ICP-MS (collection database)
  - 912 files (96 tapes, **reference set**)
  - 650 files (96 tapes**, duplicate set**)



Match criteria used for comparisons (n= 129 blind control pairs)

**The 12% of pairs that were "misclassified" by PLSDA all belong to T07 and T06 from the same package*

The elemental composition of electrical tapes analyzed by **LA-ICP-MS** provided **enhanced discrimination potential**, **improved characterization capabilities** and **stronger conclusions** than those provided by conventional methods such as SEM-EDS, as a result of their superior sensitivity, selectivity and precision.

Accuracy of elemental signatures of electrical tapes by LA-ICP-MS

$$\%\ Accuracy = \frac{true\ positives + true\ negatives}{total\ number\ of\ test\ samples} = \frac{[129 + 3760]}{4134} = \mathbf{94.1\ \%}$$

Discrimination potential of LA-ICP-MS compared to current tape methods*

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	SEM-EDS	Current methods* all	LA-ICP-MS	SEM + LA-ICP-MS	LA-ICP-MS + current methods
Percent discrimination	87.3%	94.3%	93.9%	93.9%	96.5%
Distinguished pairs	3496	3777	3757	3757	3865
Distinct groups	15	40	50	50	57
Percent indistinguishable pairs	12.7%	5.7%	6.1%	6.1%	3.5%

Current methods include physical examination, FTIR, SEM-EDS and Pyr-GC-MS
as reported for the same sample set by Mehltretter AH, Bradley MJ, and Wright DM Journal of Forensic Sciences, 2011, 56(6); 1493-1504

Conclusions and future directions

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- LA-ICP-MS has shown to be useful tool that complements current protocols for the characterization and comparison of electrical tapes and provides a good alternative for quick screening.

- Advantages of this method over SEM-EDS are:
  - Increased sensitivity that offers a more **thorough characterization** of the materials.
  - **Superior classification** of tapes to support leading investigations.
  - Enhanced selectivity that **increases confidence** in the conclusions.
  - **Improved discrimination** between tapes originating from different sources.

- Ongoing research includes the analysis of the adhesive and investigation of contamination from endogenous residues incorporated into the evidence and the evaluation of cheaper laser ablation methods such as LIBS

Acknowledgements

- Research group members that participated in this research project
  - LA-ICP-MS: Claudia Martínez
  - LIBS: Ivy Cheung
  - SEM-EDS: Melanie Perez-Montoya
- Andria Mehltretter and FBI laboratory for providing tape samples.
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- NIST
- NIJ Award 2015-DN-BX-K050

Evaluation of statistical tools for match criteria and classification

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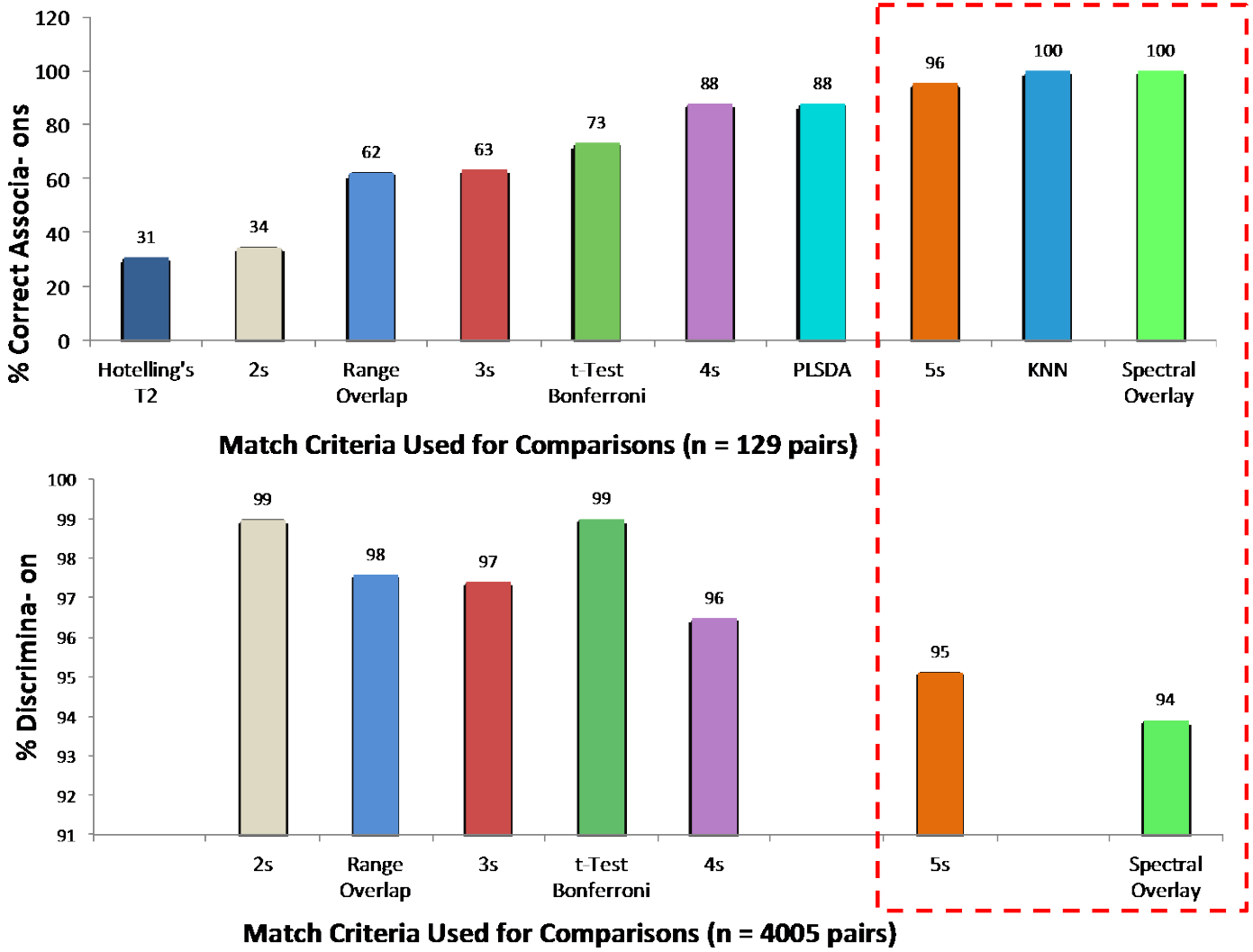
- For K/Q comparisons
  - Spectral overlay
  - Confidence intervals (2s, 3s, 4s, 5s)
  - Range overlap
  - t-test (95%, 99%, Bonferroni correction)
- For association (grouping, classification)
  - All the above and
  - PLSDA
  - KNN
  - Hotellings T^2

Evaluation of the performance of match criteria on LA-ICP-MS of tape



Statistical *methods that are selected accordingly to the spatial resolution, sensitivity and precision of the laser ablation methods as well as variations within the product, can be used to* ***estimate error rates and significance of and association or discrimination among tapes.***

PLSDA, KNN, Spectral overlay and 5s are appropriate tools for classification / association of tapes when large number of known sources are used as reference .

Broad match criteria such as spectral overlay and 5s account for inter-day, intra-day and within roll variations, providing low percent of false exclusions while still providing good discrimination between samples originating from different sources.