Implementation of Ion Beam Analysis for forensic applications: The way to Global Forensic Database through the unification of different analytical techniques

Olga Girshevitz

BINA
Bar-Ilan Institute
of Nanotechnology
& Advanced Materials
Bar-Ilan University

May 2022, Vienna

Contents

Ion Beam Analysis and Forensics:

- What do Forensic Analysts need to consider in choosing an analytical method?
- Why using Ion Beams methods for analysis in Forensics?
- Trends
- Can IBA be useful in Forensics?

Implementation of the IBA methods for unified modellable database of Car glass

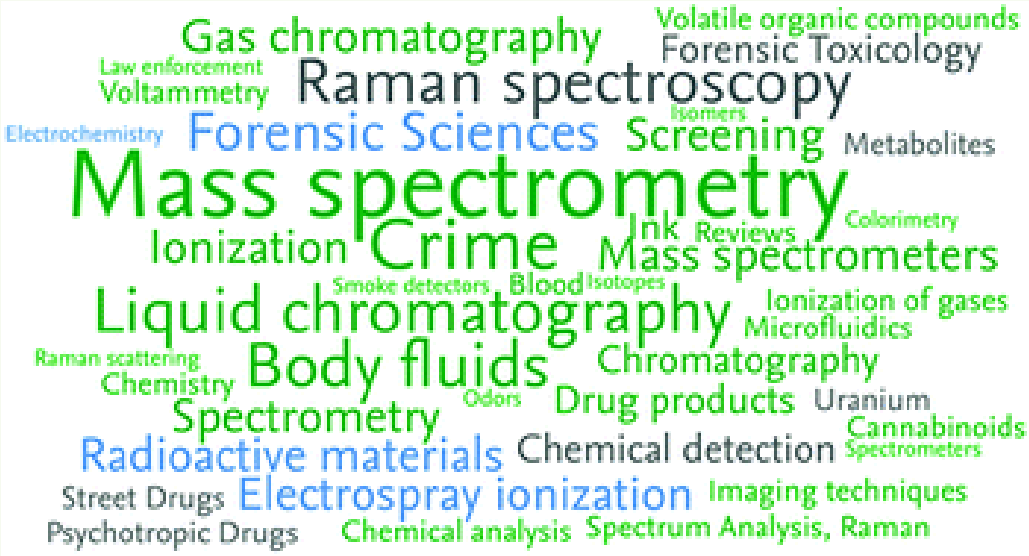
- Same analytical method (PIXE) *vs* different laboratories
- Complementary PIXE/LA-ICP-MS/PGAA/PIGE/INAA/EDS
- Combination of the various IBA techniques and Machine Learning tools as the way to a reliable classification model

Open questions

In forensic science:

1. **the work begins on the crime scene and finishes in court;**
2. **there are no magic wands;**
3. **items need to be collected, analysed and results need forensic interpretation**

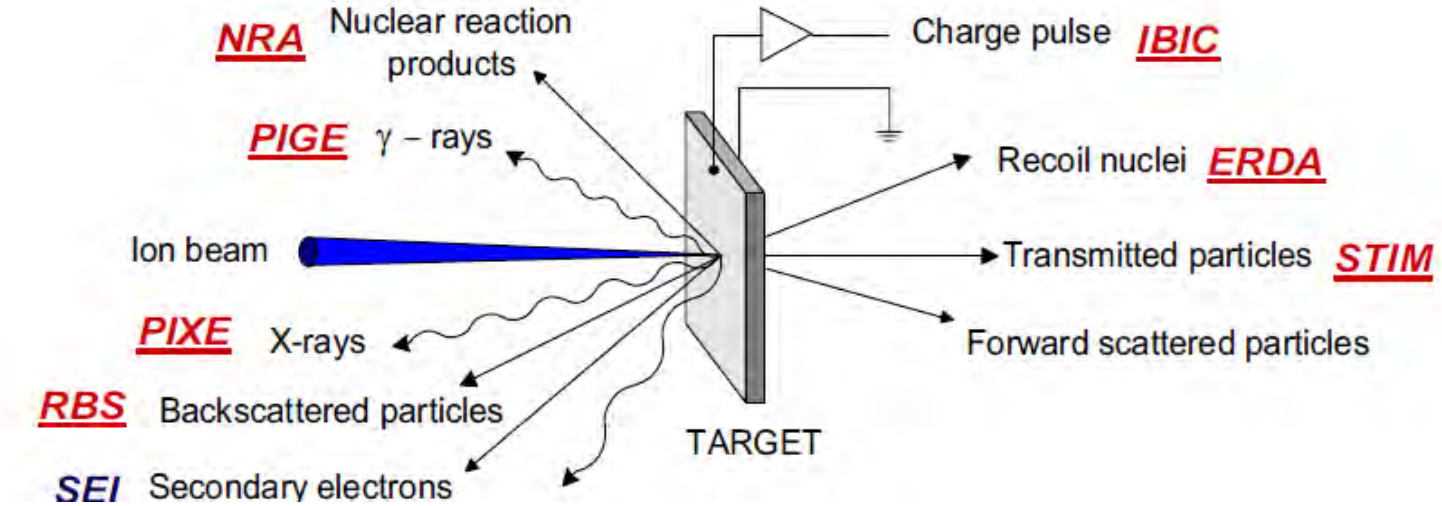
➢ What do Forensic Analysts need to consider in choosing an analytical method?



Analytical Methods,(43) 2018

- Sample size
- Destructive or non-destructive
- Availability of instrumentation, cost and operation
- Total analysis time
- Sample preparation requirements
- Quantitative or qualitative required
- What level of analysis is required (e.g., ± 1.0% or ± 0.001%)
- Detection levels and useful analytical concentration ranges
- Admissibility (e.g., are all fragments compositionally the same or are there sufficient variations among “known” fragments of the world to link two samples)

Ion Beam Analysis Methods



IBIL Ion Beam induced luminescence

Identification and quantification of the elements + depth distribution using MeV ion beams:

- ✓ PIXE
- ✓ RBS
- ✓ ERDA
- ✓ NRA

Characterization (density, charge transport, chemical bonds, morphology, crystallinity) with MeV ion beams:

- ✓ STIM (density)
- ✓ IBIC (charge transport)
- ✓ Channeling (crystallinity)
- ✓ SEI (morphology)
- ✓ IBIL (chemical bonds, impurities, structural defects)

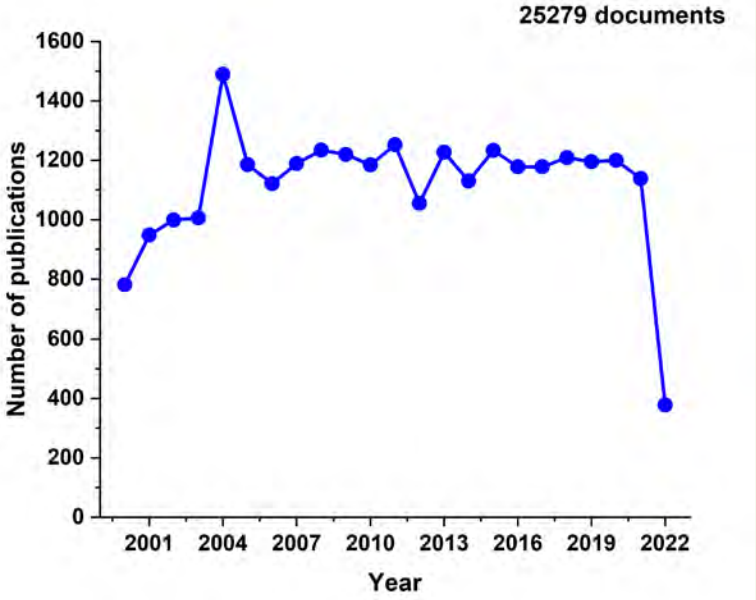
➢ Why using Ion Beams methods for analysis in Forensics?

- ✓ Non –destructive. The samples remain intact during the analysis, which means evidence or artifacts can then be further evaluated using additional methods to gather more information
- ✓ Very high sensitivity to trace elements
- ✓ Fully quantitative and absolute
- ✓ Can produce elemental maps on a sub micron scale
- ✓ Measurements in vacuum or in air
- ✓ Accurate / reproducible
- ✓ Highly discriminating
- ✓ Need no sample preparation

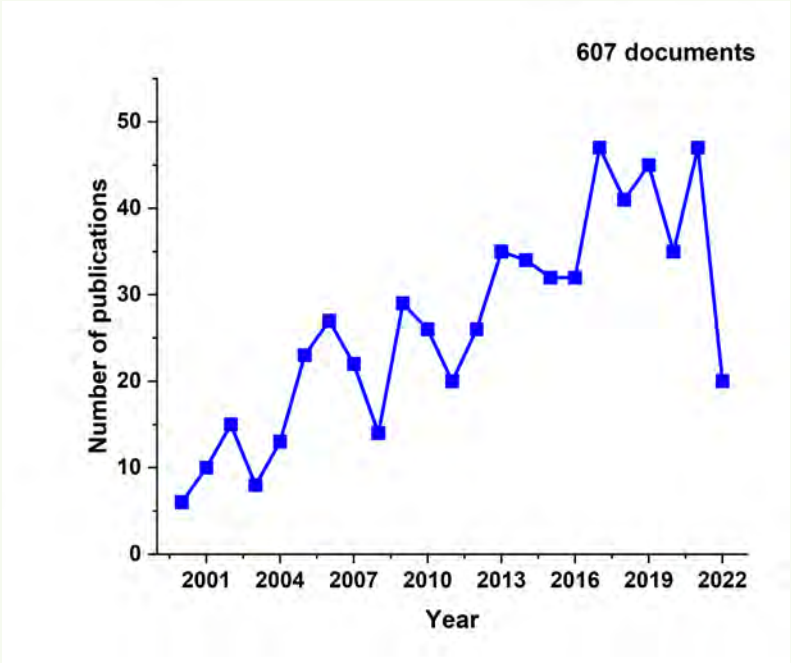
Negative points:

- ✓ Not portable
- ✓ Not reasonable time
- ✓ Not cheap

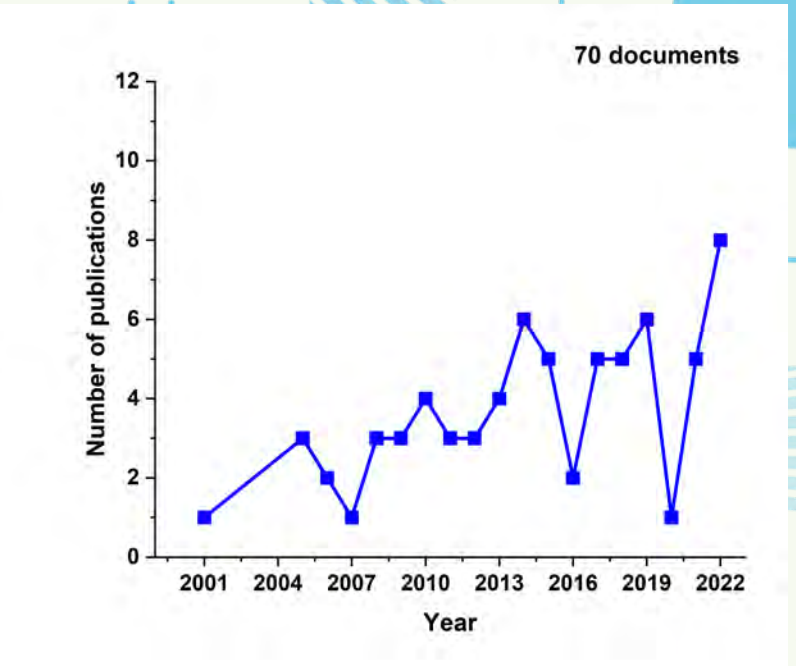
IBA and Forensics: trends



Results of SCOPUS search with topic “IBA“



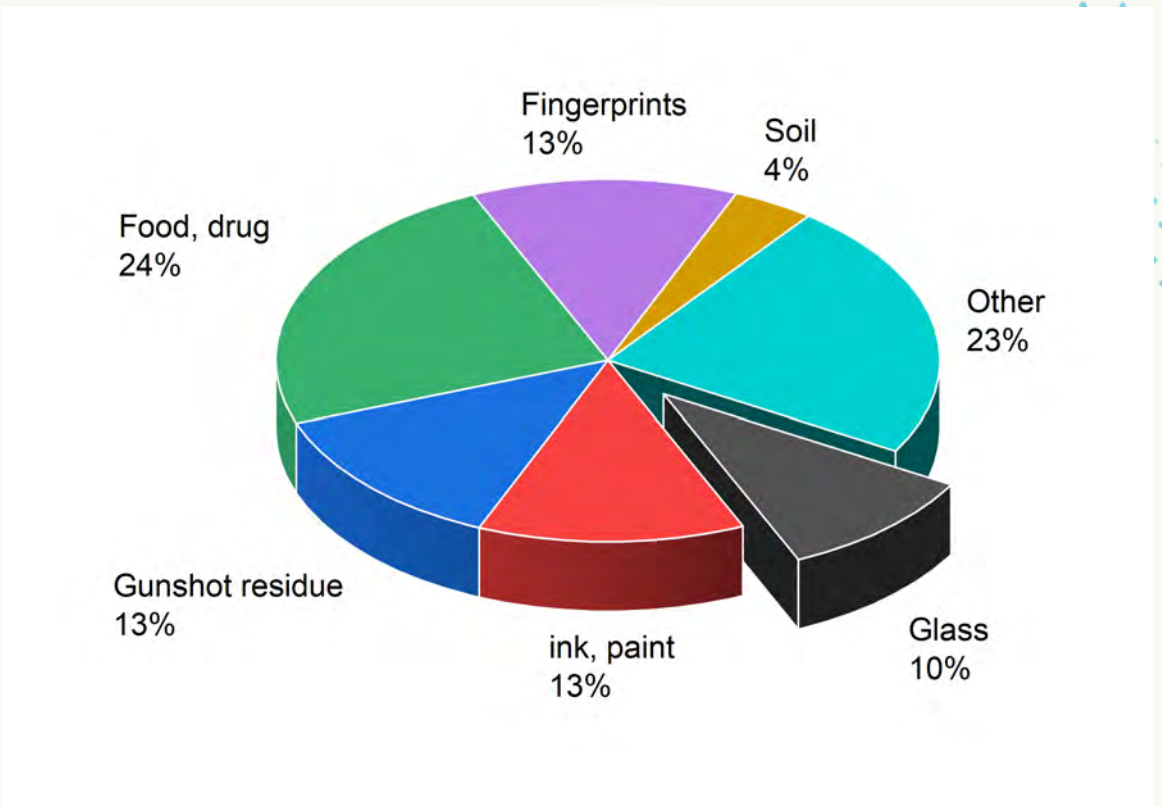
Results of SCOPUS search with topics “elemental analysis” and “ forensic”



Results of search with topics “forensic” and “IBA“

0.3% from the all IBA publications
11.4% from the all publications that include topics “elemental analysis” and “forensic”

➢ Can IBA be useful in Forensics?



Results of SCOPUS search demonstrate % of the different forensic materials that were analyzed by "IBA" in the period between 2000-2022

Can IBA be useful in Forensics?

Nuclear Instruments and Methods in Physics Research B 268 (2010) 1929–1932

Contents lists available at ScienceDirect

Nuclear Instruments and Methods in Physics Research B

journal homepage: www.elsevier.com/locate/nimb

Depth profiling of fingerprint and ink signals by SIMS and MeV SIMS

M.J. Bailey [a,*], B.N. Jones [a], S. Hinder [b], J. Watts [b], S. Bleay [c], R.P. Webb [a]

[a] University of Surrey Ion Beam Centre, Surrey GU2 7XH, UK
[b] Surface Analysis Laboratory, University of Surrey, GU2 7XH, UK
[c] Home Office Scientific Development Branch, St. Albans, UK

Forensic Science International 331 (2022) 111136

Contents lists available at ScienceDirect

Forensic Science International

journal homepage: www.elsevier.com/locate/forsciint

Comparison of optical techniques and MeV SIMS in determining deposition order between optically distinguishable and indistinguishable inks from different writing tools

Marko Barac [a,*], Andrijana Filko [b], Zdravko Siketić [a], Marko Brajković [a], Andrea Ledić [b], Iva Bogdanović Radović [a]

[a] Division of Experimental Physics, Ruđer Bošković Institute, Bijenička 54, 10000 Zagreb, Croatia
[b] Forensic Science Centre "Ivan Vučetić", Ilica 335, 10000 Zagreb, Croatia

- SIMS and MeV SIMS used in determination of the deposition order of a doped fingerprint and written text
- the sequence can be determined with MeV SIMS
- the problem arises for real case fingerprints which are developed by fingerprint reagents

- MeV SIMS used in correlation with optical techniques for distinguishing inks in writing tools
- added value in determining the deposition order and ink line intersections
- MeV SIMS more efficient for distinguishing oil-based inks

Can IBA be useful in Forensics?

Forensic Science International 231 (2013) 219–228

Contents lists available at SciVerse ScienceDirect

Forensic Science International

journal homepage: www.elsevier.com/locate/forsciint

Integrated Ion Beam Analysis (IBA) in Gunshot Residue (GSR) characterisation

F.S. Romolo [a,b,*], M.E. Christopher [c], M. Donghi [d], L. Ripani [e], C. Jeynes [c], R.P. Webb [c], N.I. Ward [f], K.J. Kirkby [c], M.J. Bailey [f]

[a] Dipartimento di Scienze Anatomiche, Istologiche, Medico-Legali e dell'Apparato Locomotore, SAPIENZA Università di Roma, Italy
[b] Institut de Police Scientifique, Université de Lausanne, Switzerland
[c] Surrey Ion Beam Centre, University of Surrey, Guildford, Surrey GU2 7XH, United Kingdom
[d] Reparto Investigazioni Scientifiche Carabinieri, Parma, Italy
[e] Reparto Investigazioni Scientifiche Carabinieri, Roma, Italy
[f] Department of Chemistry, University of Surrey, Guildford, Surrey GU2 7XH, United Kingdom

- IBA in conjunction with SEM-EDS
- PIXE – added value: lower detection limit than EDS; detection of Hg from the mercury fulminate primers
- PIGE – added value: identification of light elements, boron and sodium

PLOS ONE

RESEARCH ARTICLE

Molecular imaging of humain hair with MeV-SIMS: A case study of cocaine detection and distribution in the hair of a cocaine user

Luka Jeromel[1], Nina Ogrinc[2¤], Zdravko Siketić[3], Primož Vavpetič[1], Zdravko Rupnik[1], Klemen Bučar[1], Boštjan Jenčič[1], Mitja Kelemen[1], Matjaž Vencelj[1], Katarina Vogel-Mikuš[1,4], Janez Kovač[1], Ron M. A. Heeren[2], Bryn Flinders[2], Eva Cuypers[2,5], Žiga Barba[1]*, Primož Pelicon[1]

1 Jožef Stefan Institute, SI-Ljubljana, Slovenia, 2 The Maastricht MultiModal Molecular Imaging Institute, Maastricht University, ER Maastricht, Maastricht, The Netherlands, 3 Rudjer Bošković Institue, Zagreb, Croatia, 4 Department of Biology, Biotechnical Faculty, University of Ljubljana, Ljubljana, Slovenia, 5 KU Leuven Toxicology & Pharmacology, Leuven, Belgium

¤Current address: Univ. Lille, Inserm, CHU Lille, U1192 - Protéomique Réponse Inflammatoire Spectrométrie de Masse – PRISM, Lille, France
* ziga.barba@ijs.si

- MeV SIMS used for determination of the cocaine concentration profile along the growth axis of human hair
- High chemical sensitivity and non-destructive characterization
- Ability to reconstruct a detailed history of cocaine intake

Can IBA be useful in Forensics?

Talanta 224 (2021) 121829

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Ion beam analysis (IBA) and instrumental neutron activation analysis (INAA) for forensic characterisation of authentic Viagra® and of sildenafil-based illegal products

Francesco Saverio Romolo [a,*], Mehmet Sarilar [b], Johann Antoine [c], Serena Mestria [d], Sabina Strano Rossi [d], Matteo Davide Gallidabino [e], Guilherme Maurício Soares de Souza [f], Paola Chytry [f], Johnny Ferraz Dias [f]

[a] Department of Law, Università degli Studi di Bergamo, Italy
[b] Reactor Institute Delft, University of Technology Delft, the Netherlands
[c] Nuclear Analytical Laboratory, International Centre for Environmental and Nuclear Sciences, University of the West Indies, Mona Campus, Kingston, Jamaica
[d] Forensic Toxicology Laboratory, Department of Health Surveillance and Bioethics, F. Policlinico Gemelli IRCCS Roma - Università Cattolica del Sacro Cuore, Italy
[e] Centre for Forensic Science, Department of Applied Sciences, Faculty of Health & Life Sciences, Northumbria University, Newcastle upon Tyne, UK
[f] Ion Implantation Laboratory, Institute of Physics, Federal University of Rio Grande do Sul, Porto Alegre, RS, Brasil

Forensic Science International 335 (2022) 111282

Contents lists available at ScienceDirect

Forensic Science International

journal homepage: www.elsevier.com/locate/forsciint

A forensic procedure based on GC–MS, HPLC-HRMS and IBA to analyse products containing sildenafil or the doping agent oxandrolone

Serena Mestria [a], Massimo Chiari [b,*], Francesco Saverio Romolo [c], Sara Odoardi [a], Sabina Strano Rossi [a]

[a] Forensic Toxicology Laboratory, Department of Health Surveillance and Bioethics, F. Policlinico Gemelli IRCCS Roma - Università Cattolica del Sacro Cuore, Italy
[b] INFN Division of Florence, via G. Sansone 1, 50019 Sesto Fiorentino, Italy
[c] Department of Law, Università degli Studi di Bergamo, Italy

- IBA – PIXE and MeV SIMS successful discrimination between the legal and illegal products
- INAA – elemental quantification and future implementation of an interlaboratory classification system

Non-destructive vs destructive

preserving the integrity of the samples is mandatory!

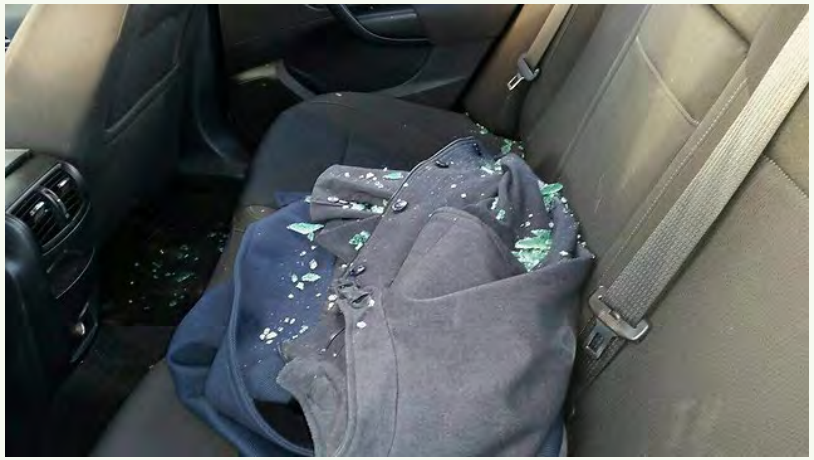
- IBA (PIXE and PIGE) in conjunction GC-MS and HPLC-HRMS
- added value of IBA – light (PIGE) and heavy elements (PIXE) determination for discrimination between legal and illegal products
- Foundation for an inter-laboratory classification system based on chromatography, MS and IBA measurements

Car glass classification by IBA methods as a part of the forensic workflow

Every year, the Israeli Police Force reports on dozens of crimes that involved glass fragment as evidence which did not realize their forensic potential.

Forensic problem

One of the frequent forensic problems is linking of the evidence to the crime scene.



Glass characterization parameters:

- **Size**
- **Color**
- **Refractive Index (RI)**
- **Elemental composition*****

*****Difficulty**: Improvement in glass manufacturing techniques and higher standard rigidity

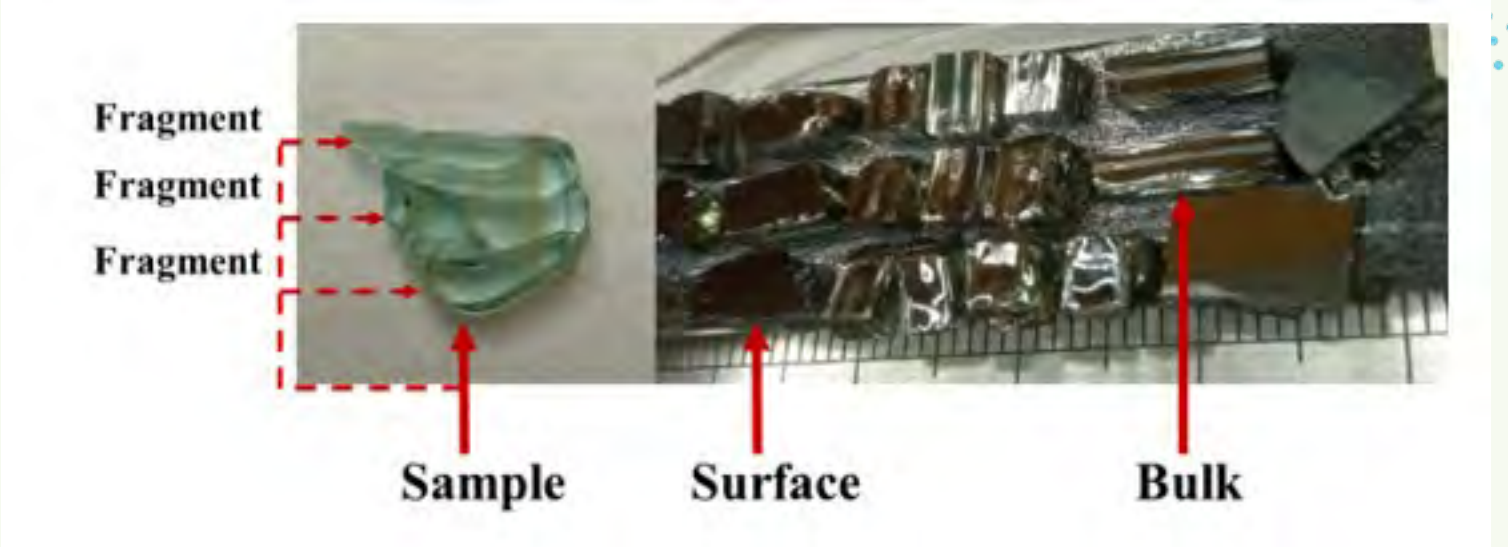
"This fragment came from a Ford!"

In the previous episodes:

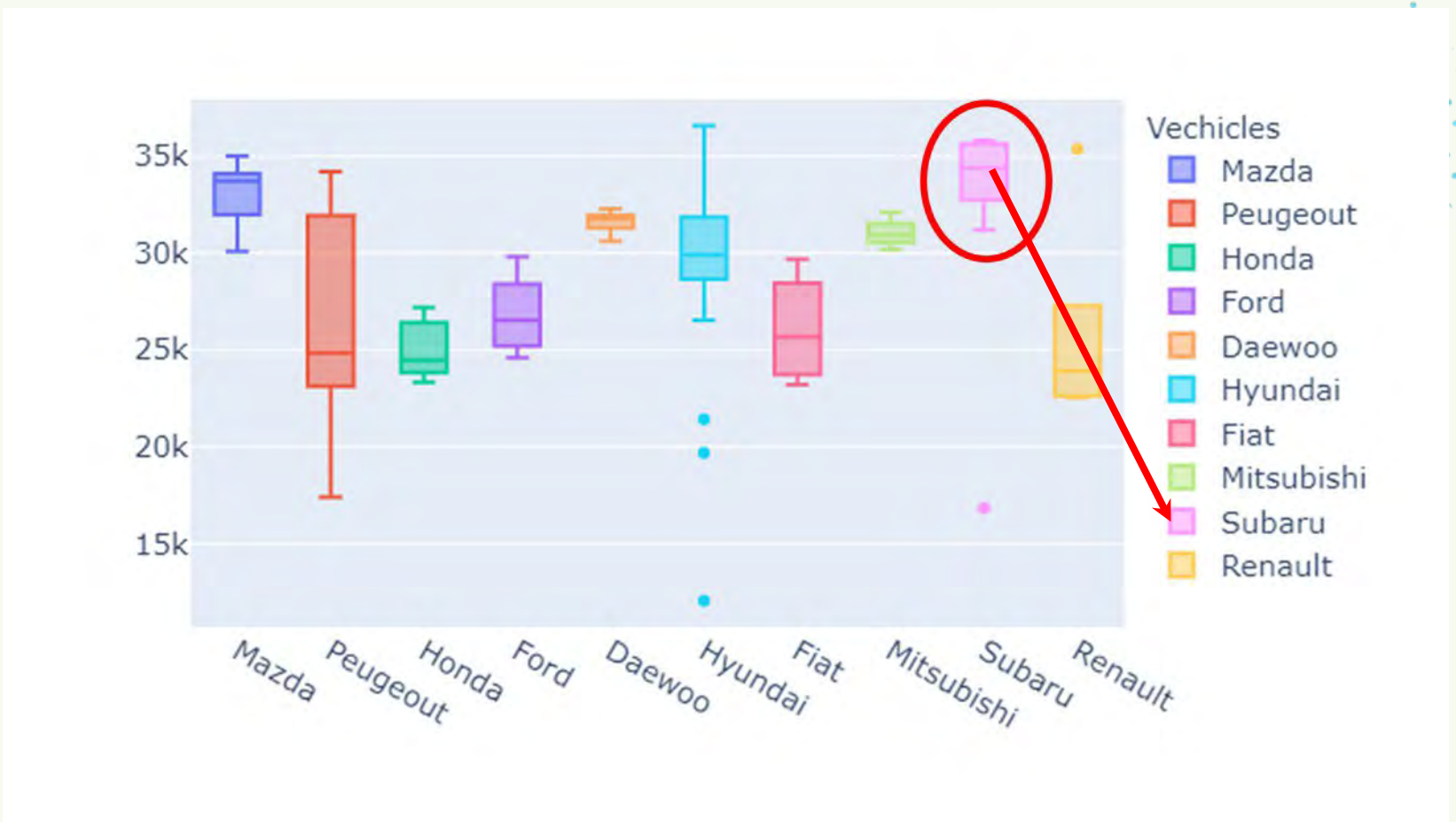
Israel Police HQ, Toolmarks and Materials Lab provided:

48 Samples:

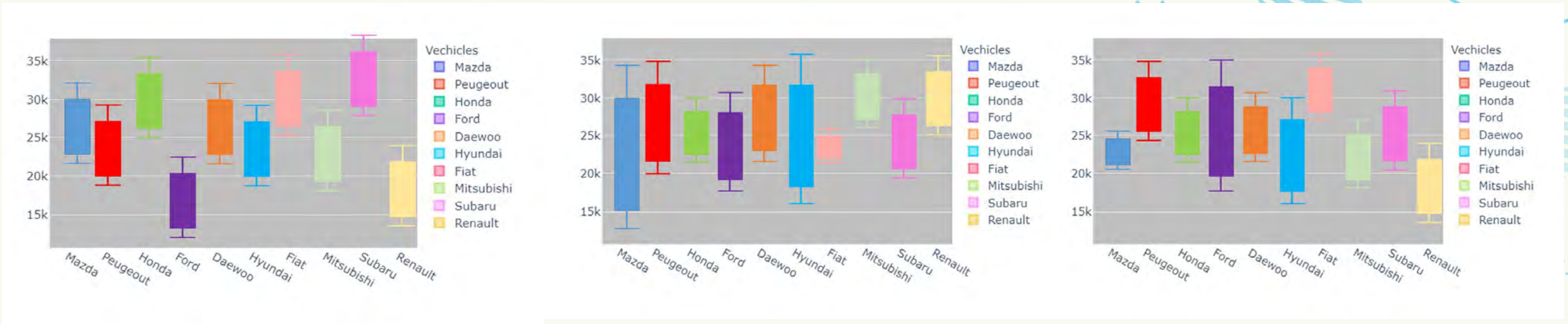
- 13 vehicles
- 10 car manufacturers



Amount of the specific element (K) as a differentiator

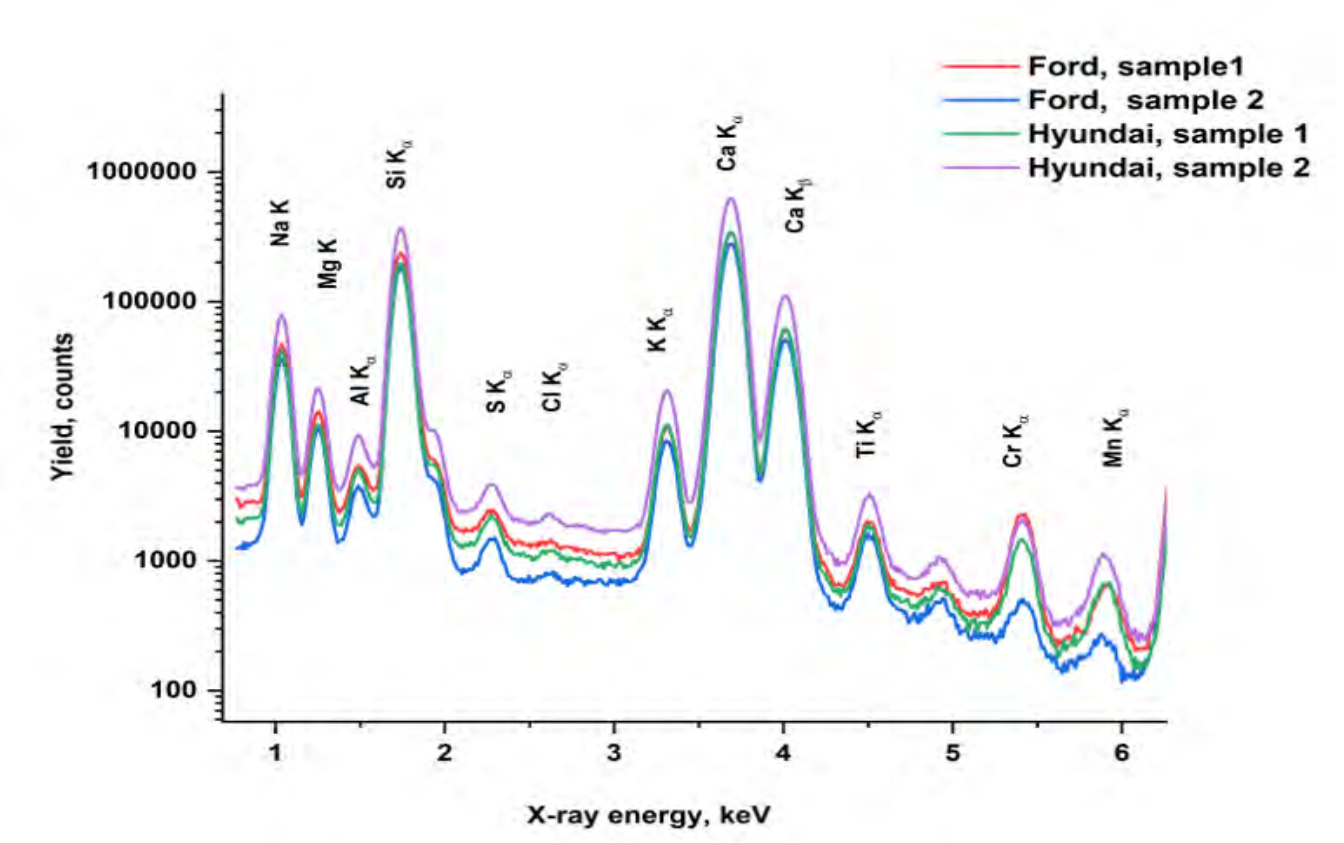


The boxplot represent the distribution of a single element, K, partitioned by manufactures



If a manufacture doesn’t display distinct differences in any of the elements, it will not be distinguished.

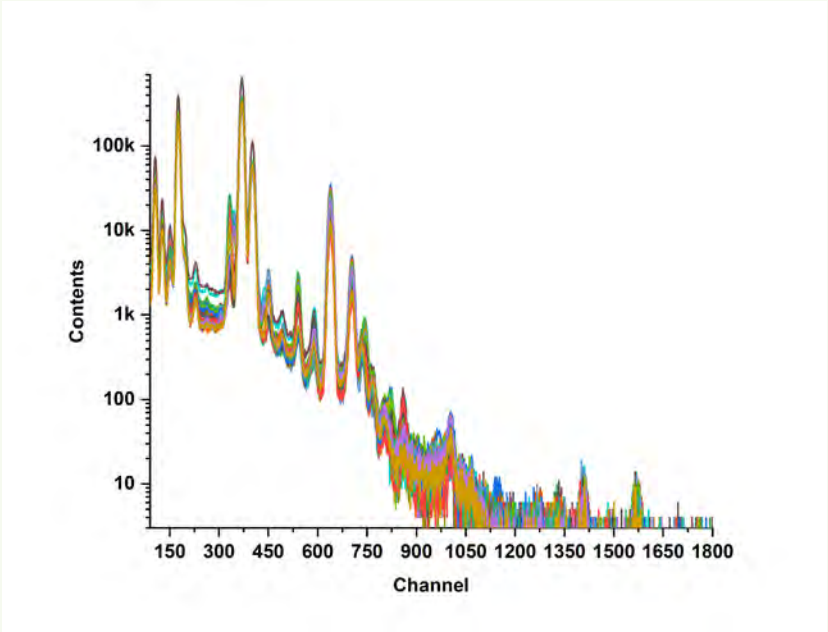
Is a big picture informative enough?



….no particular orderliness between manufacturers

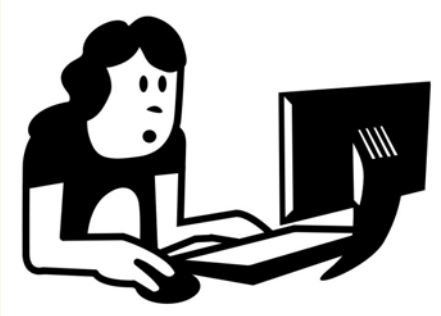
When Human learning has fails, one moves on to Machine Learning (ML)

The idea behind ML



70% - to study

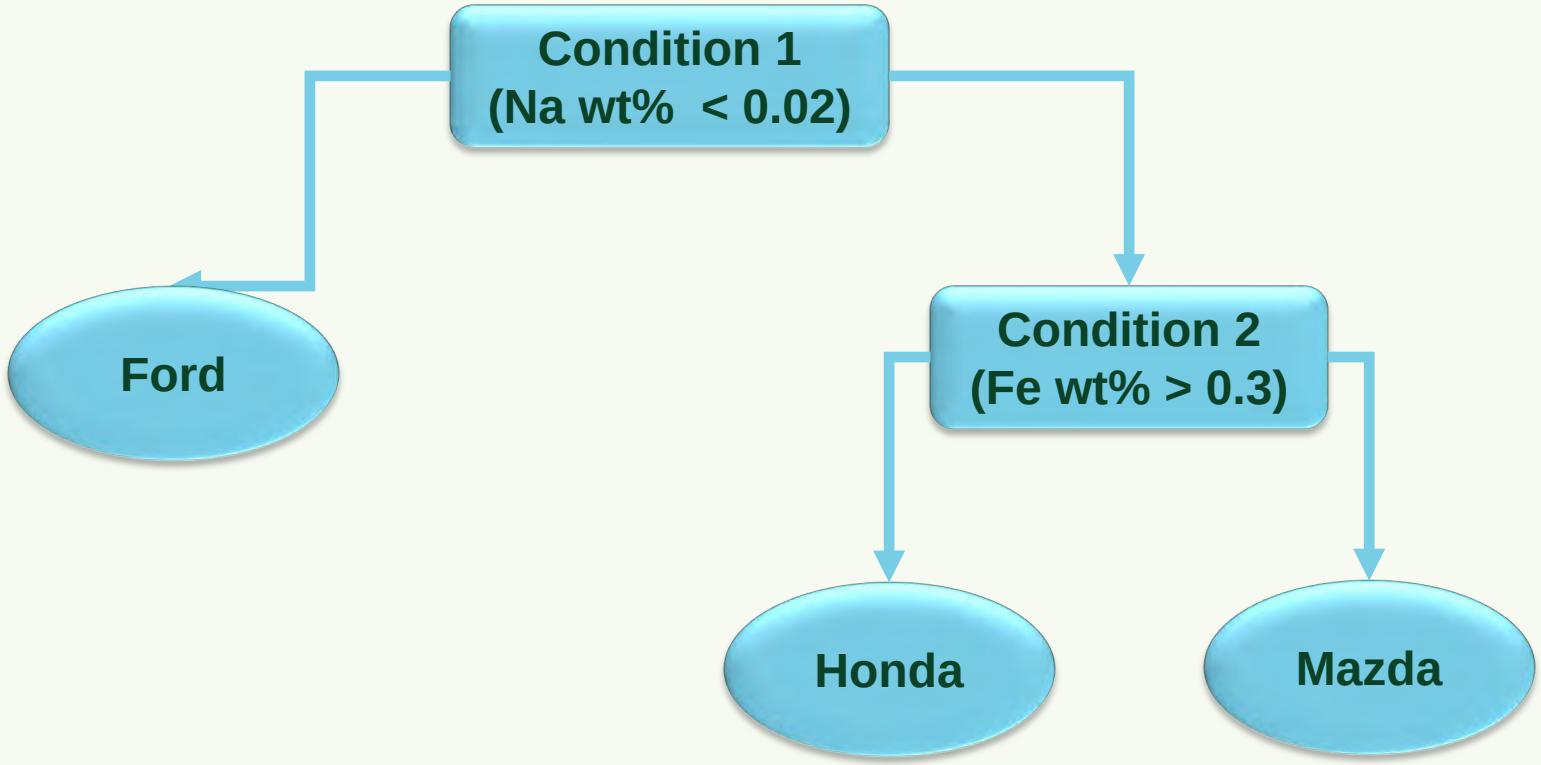
30% - to test



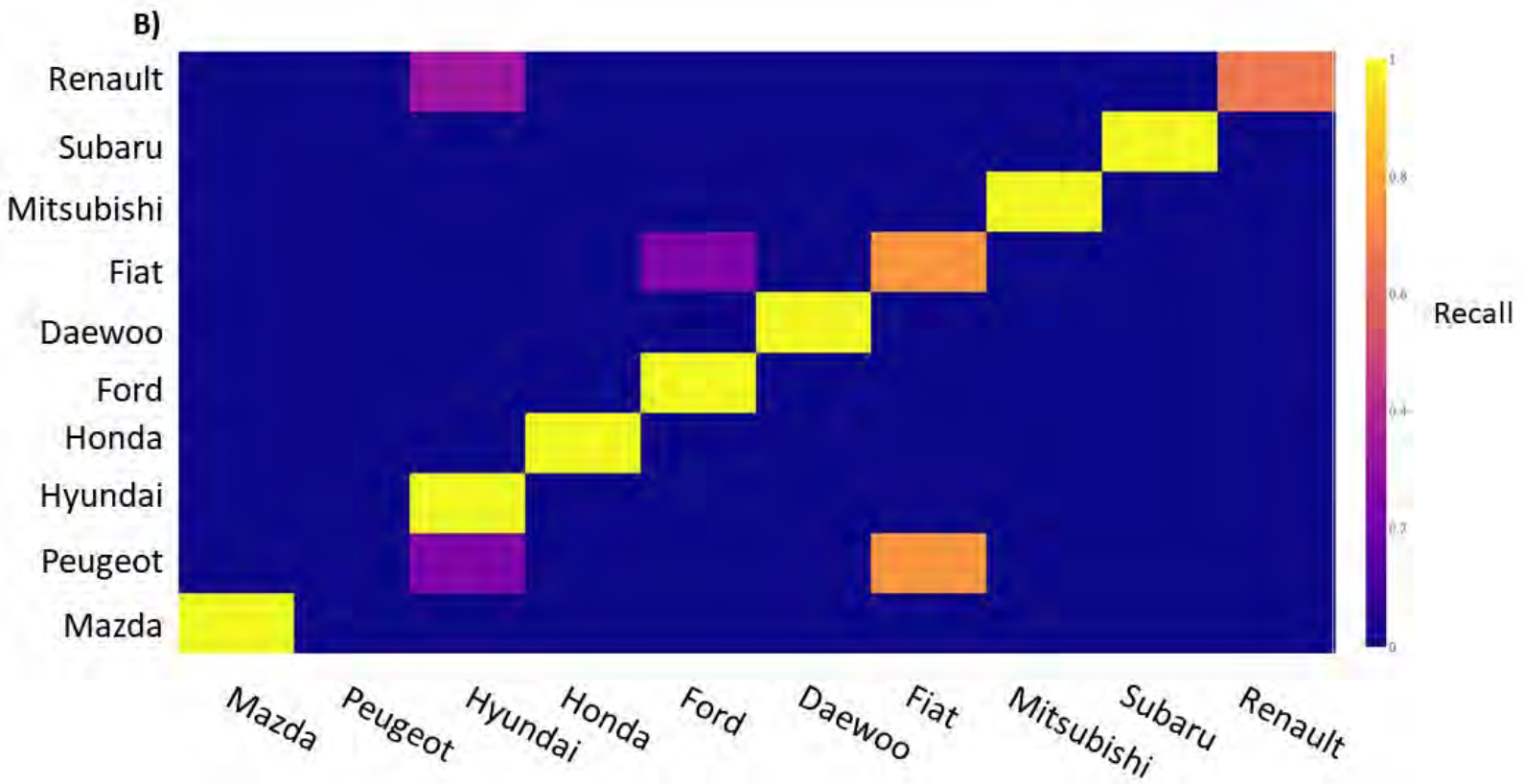
Evaluation of model on test set

The idea behind ML

Decision Tree (Machine Learning Algorithm)



New approach: Combination of two worlds – PIXE+ML



Talanta 234 (2021) 122608

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

PIXE based, Machine-Learning (PIXEL) **supported workflow for glass fragments classification**

Omer Kaspi [a], Olga Girshevitz [b,**], Hanoch Senderowitz [a,*]

[a] Department of Chemistry, Bar-Ilan University, Ramat-Gan, 5290002, Israel
[b] Bar Ilan Institute of Nanotechnology and Advanced Materials, Bar-Ilan University, Ramat-Gan, 5290002, Israel

The combination of PIXE-based elemental analysis with ML algorithms can provide reliable models for assigning glass fragments taken from cars' windshields to one of several car manufacturers

Confusion matrix demonstrates the performances of the classification model, % of correctly identified samples class.

In the next episodes:

Rule of thumb for data analysis:

"The more the merrier"

And that's why lab cooperation and information sharing is important

A global forensic database

In the next episodes:

The same samples were given to

Division of Experimental Physics
Ruđer Bošković Institute, RBI

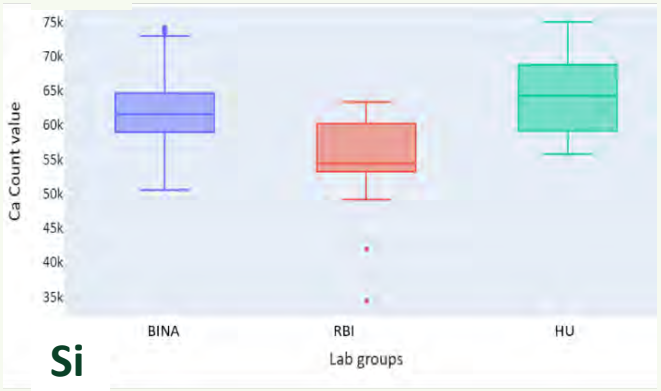
Department of Chemistry and
Institute of Nanotechnology
Bar-Ilan University, BINA

Department of Physics
University of Helsinki, HU

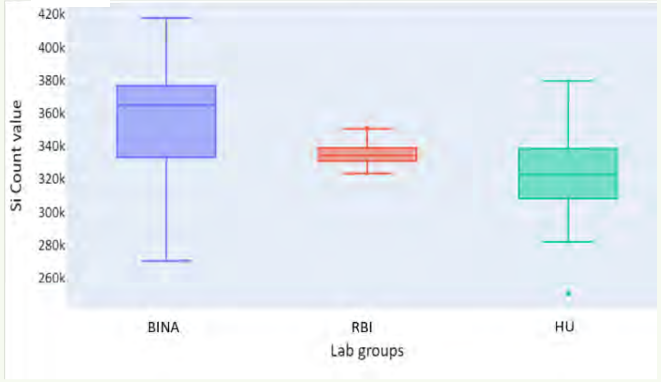
Intercomparison between PIXE results of different laboratories

Train set – RBI data, test – BINA data → **Result was not spectacular**

Ca

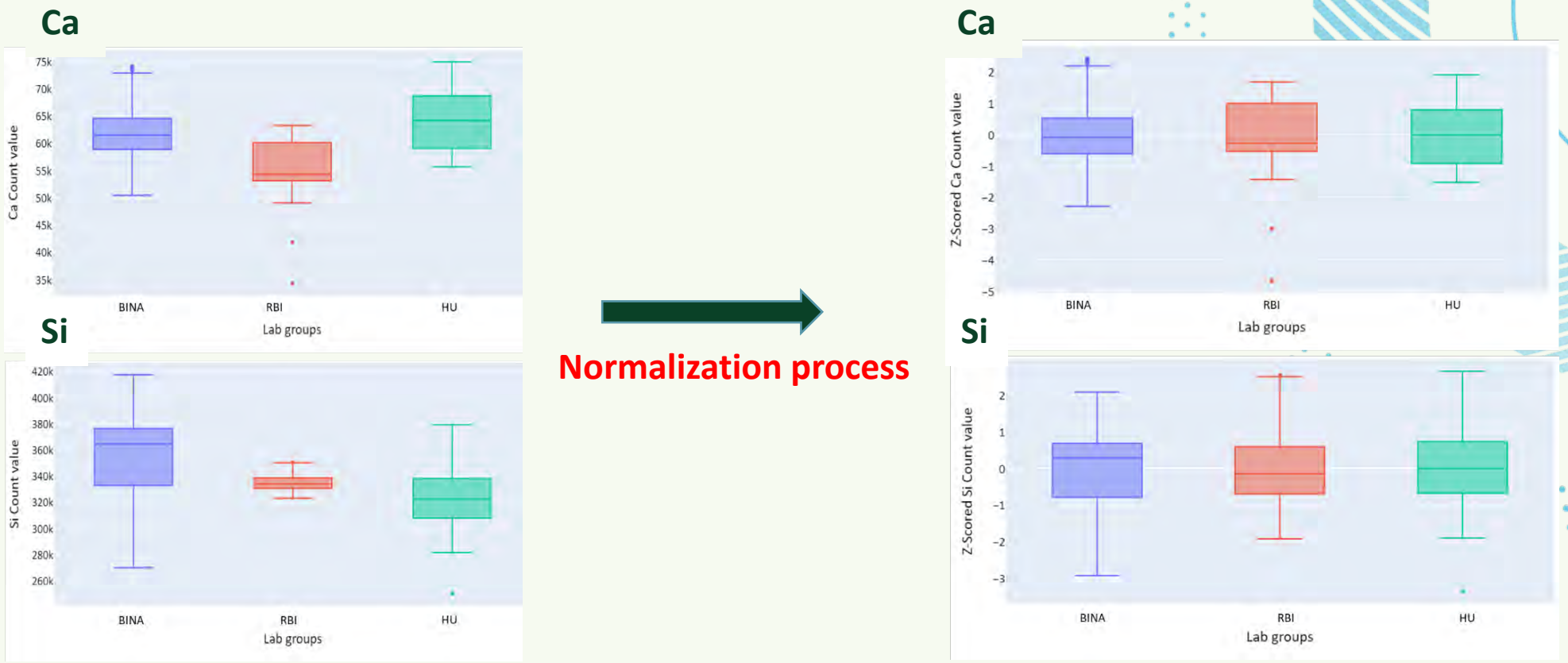


Si



The measurements were performed using the different experimental setups

Intercomparison between PIXE results of different laboratories

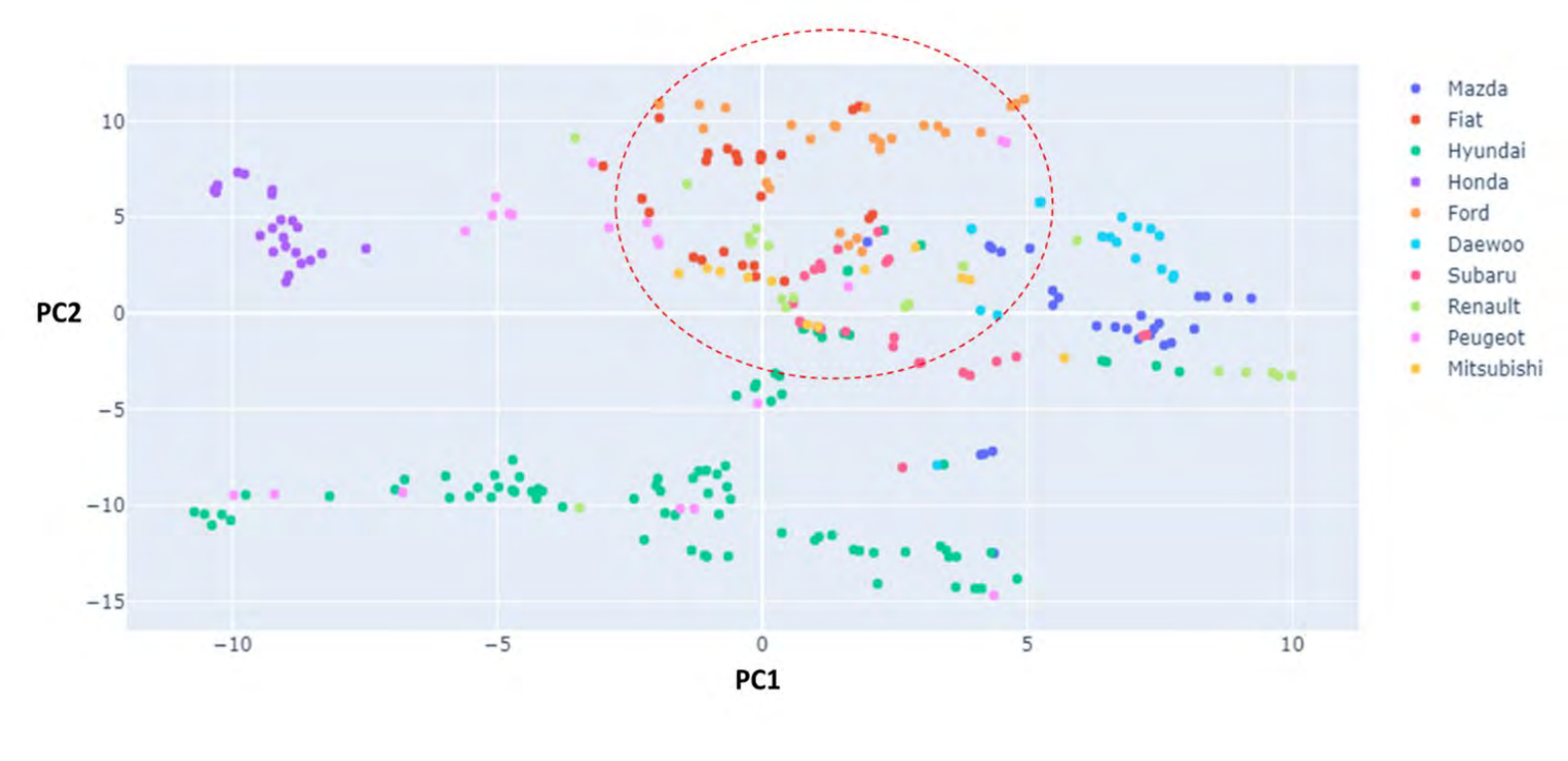


Comparison of measurements with different setups before (left) and after (right) normalization.

Normalization of the data reduces variability that is caused by different measurement protocols and instruments.

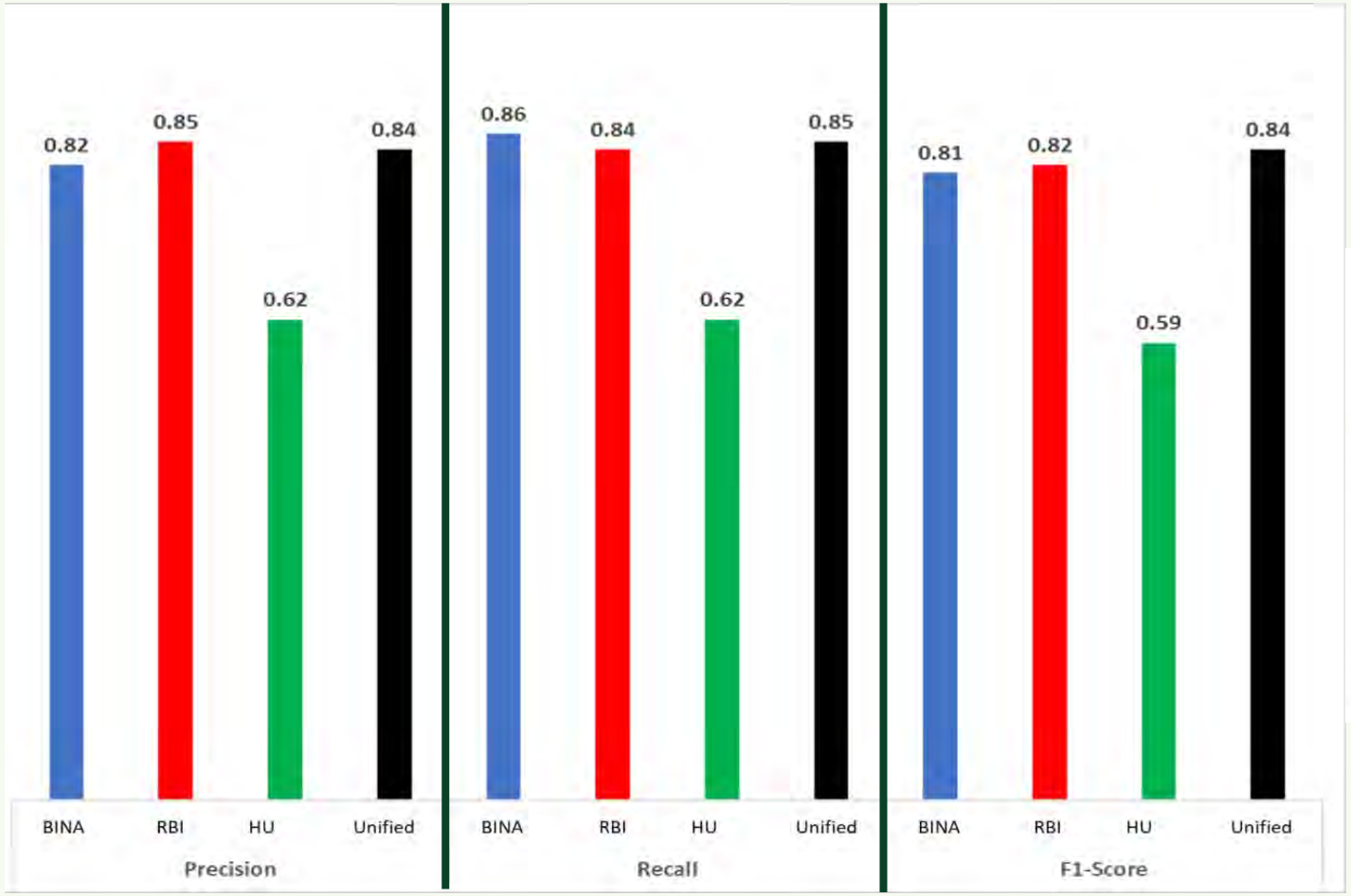
Combination of PIXE results from different laboratories to unified database

The samples from the same manufacture are located in the same area , indifferent of the measuring lab.



Dimensionality reduction of the combined database using t-SNE method.

The power of the combining results



Forensic Science International 333 (2022) 111216

Contents lists available at ScienceDirect

Forensic Science International

journal homepage: www.elsevier.com/locate/forsciint

Inter-laboratory workflow for forensic applications: Classification of car glass fragments

Omer Kaspi[a], Osnat Israelsohn-Azulay[b], Yigal Zidon[b], Hila Rosengarten[b], Matea Krmpotić[c], Sabrina Gouasmia[c], Iva Bogdanović Radović[c], Pasi Jalkanen[d], Anna Liski[d], Kenichiro Mizohata[d], Jyrki Räisänen[d], Olga Girshevitz[e,*], Hanoch Senderowitz[a,*]

[a] Department of Chemistry, Bar-Ilan University, Ramat-Gan 5290002, Israel
[b] Israel Police HQ, Toolmarks and Materials Lab, Israel
[c] Laboratory for Ion Beam Interactions, Division of Experimental Physics, Ruđer Bošković Institute, Bijenička cesta 54, HR-10000 Zagreb, Croatia
[d] Department of Physics, University of Helsinki, P.O. Box 43, FI-00014 Helsinki, Finland
[e] Bar Ilan Institute of Nanotechnology and Advanced Materials, Bar-Ilan University, Ramat-Gan 5290002, Israel

The model produced by the uniform database has performances metrics values equal or better of the best performing lab-specific model.

The last episode:

Classification of glass specimen using multiple analytical techniques measured in multiple laboratories

Laboratories	Alternate/Complement techniques
BINA, Israel	PIXE
HU, Finland	PIXE
RBI, Croatia	PIXE
DIFS, Israel	EDS
ATOMKI, Hungary	LA ICP-MS
BNC, Hungary	PGAA
BARC, India	INAA, PIGE

Performances of lab-specific models

Lab group/method	Precision	Recall	F1 - Score
BINA / PIXE	0.84 ± 0.05	0.88 ± 0.05	0.83 ± 0.05
RBI / PIXE	0.84 ± 0.05	0.87 ± 0.05	0.83 ± 0.05
HU / PIXE	0.65 ± 0.08	0.66 ± 0.13	0.61 ± 0.10
BARC / INAA, PIGE	0.92 ± 0.06	0.87 ± 0.10	0.89 ± 0.08
BNC / PGAA	0.52 ± 0.25	0.48 ± 0.26	0.49 ± 0.25
ATOMKI / LA-ICP MS	0.79 ± 0.09	0.76 ± 0.12	0.76 ± 0.10
DIFS / EDS	0.51 ± 0.09	0.52 ± 0.11	0.48 ± 0.10

Samples Collection: 48 glass specimens from 13 different car models from 10 car manufacturers were collected and recorded. The same specimens that were previously measured by PIXE were now provided to all labs for analysis by other techniques

Agreement between labs on features' importance

Chosen by:	BINA, PIXE	RBI, PIXE	HU, PIXE	BARC, PIGE +INAA	BNC, PGAA	ATOMKI, LA ICP-MS	DIFS EDS
K	X	X	X	*	X		X
Al	X	X	X		X		X
Ti	X	*	X	*	X		*
Fe	X	X	X		X	X	X
Mn	X	X	*	*			*
Ca	X	X	X		*	X	*
Mg		X	*				X
Zn	X	*	*	X	*		*
Si		X	X		X		X
Cr		X	*		*	*	*
S		X	*	*	*	*	*
Na		X	*		X		X
Ce, Zr, Rb, Eu	*	*	*	X	*		*
Sc, Co	*	*	*	X	*	*	*
La	*	*	*	X	*	X	*
Gd, B	*	*	*	*	X		*
Cl	*	*	*	*	X	*	*
Pr, As, Bi	*	*	*	*	*		*

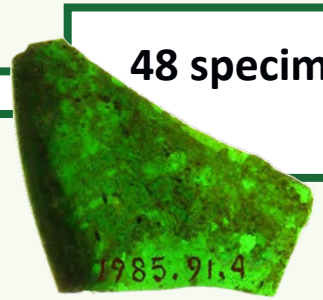
X - features that were measured and found among the ten topmost important features.

Empty cells - features that were measured but not determined to be within the ten topmost important features.

* - elements that were not measured by the specific lab.

How can we get better?

Data Base
496 measurements

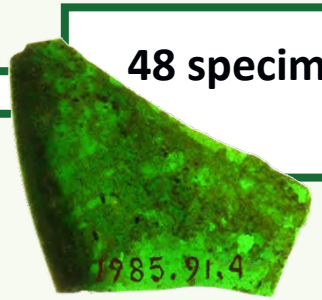


Si, Al, Ca, Fe

These features are common to all laboratories

Precision – 0.68±0.03
Recall - 0.67±0.03
F1-Score - 0.66±0.04

Data Base
284 measurements
(without BNC, DIFS, HU)



Si, Al, Mg, Na, Ca, Fe

The data from laboratories with performance values <70% were discarded (BNC, DIFS and HU).

Precision – 0.82±0.03
Recall - 0.79±0.03
F1-Score - 0.79±0.04

How can we get better?

Performances of models derived from combinations of different techniques

	PIXE	PIGE +INAA	LA-ICP-MS	EDS
PIXE	P: 0.87±0.04 R: 0.90±0.03 F1: 0.87±0.05	P: 0.78±0.05 R: 0.81±0.04 F1: 0.77±0.05	P: 0.92±0.02 R: 0.93±0.02 F1: 0.92±0.03	P: 0.81±0.04 R: 0.84±0.03 F1: 0.81±0.05
PIGE + INAA		P: 0.92±0.06 R: 0.87 ± 0.10 F1: 0.89 ± 0.08	P: 0.86±0.06 R: 0.83 ± 0.09 F1: 0.83 ± 0.07	P: 0.49±0.06 R: 0.50 ± 0.09 F1: 0.46 ± 0.07
LA-ICP-MS			P: 0.79±0.09 R: 0.76 ± 0.12 F1: 0.76 ± 0.10	P: 0.88±0.06 R: 0.89 ± 0.06 F1: 0.86 ± 0.07
EDS				P: 0.51±0.09 R: 0.52 ± 0.11 F1: 0.48 ± 0.10

- **Combining measurements from two labs leads to models which are significantly better than the lower-performing model of the two labs and are only slightly worse than the higher-performing model.**
- **BARC produces high quality classification models using a completely different features set than used by all other methods**

In order to participate in the unified DB it is not sufficient for it to be able to properly measure samples and construct a good predictive model but also to be able to construct good predictive models using the important features as determined by other labs.

For the next episodes, open questions are:

- Will model performances be improved if models will be derived from the raw spectra?
- Can the model application be expended to identify glasses that do not origin from vehicles? Or other forensic materials?
- Is it feasible to create a web-based database? And to use it as new reference to point out specific differences in the results that come from specific laboratories?

The most work on the glass was carried out under the IAEA Coordinated Research Project on “Enhancing Nuclear Analytical Techniques to Meet the Needs of Forensic Sciences” (F11021), 2017-2021

BINA Team	RBI Team	HU Team	BNC Team	BARC Team	ATOMKI Team	Israeli Police
Olga Girshevitz	Iva Bogdanović Radović	Jyrki Räisänen	Zsolt Kasztovszkye	Raghunath Acharya	Molnár Mihály ,	Amit Haliva
Hanoch Senderowitz	Matea Krmpotić	Pasi Jalkanen	Ildikó Harsányie	Pradeep K. Pujari	Mihaly Braun	Osnat Israelsohn-Azulay
Omer Kaspi	Sabrina Gouasmia	Anna Liski				Zidon Yigal
		Kenichiro Mizohata				Hila Rosengarten
						Yaron Cohen
						Tsach Tsadok

Special thanks to Aliz Simon and Nuno Barradas for the helpful discussions and support

Thank you!

Combining Elemental Analysis and Machine Learning