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Assoc. Prof. **Pavel Pořízka**, Ph.D.

Laser spectroscopy as an advanced sensor in polymer recycling

IFATI4-2021 November 8, 2021

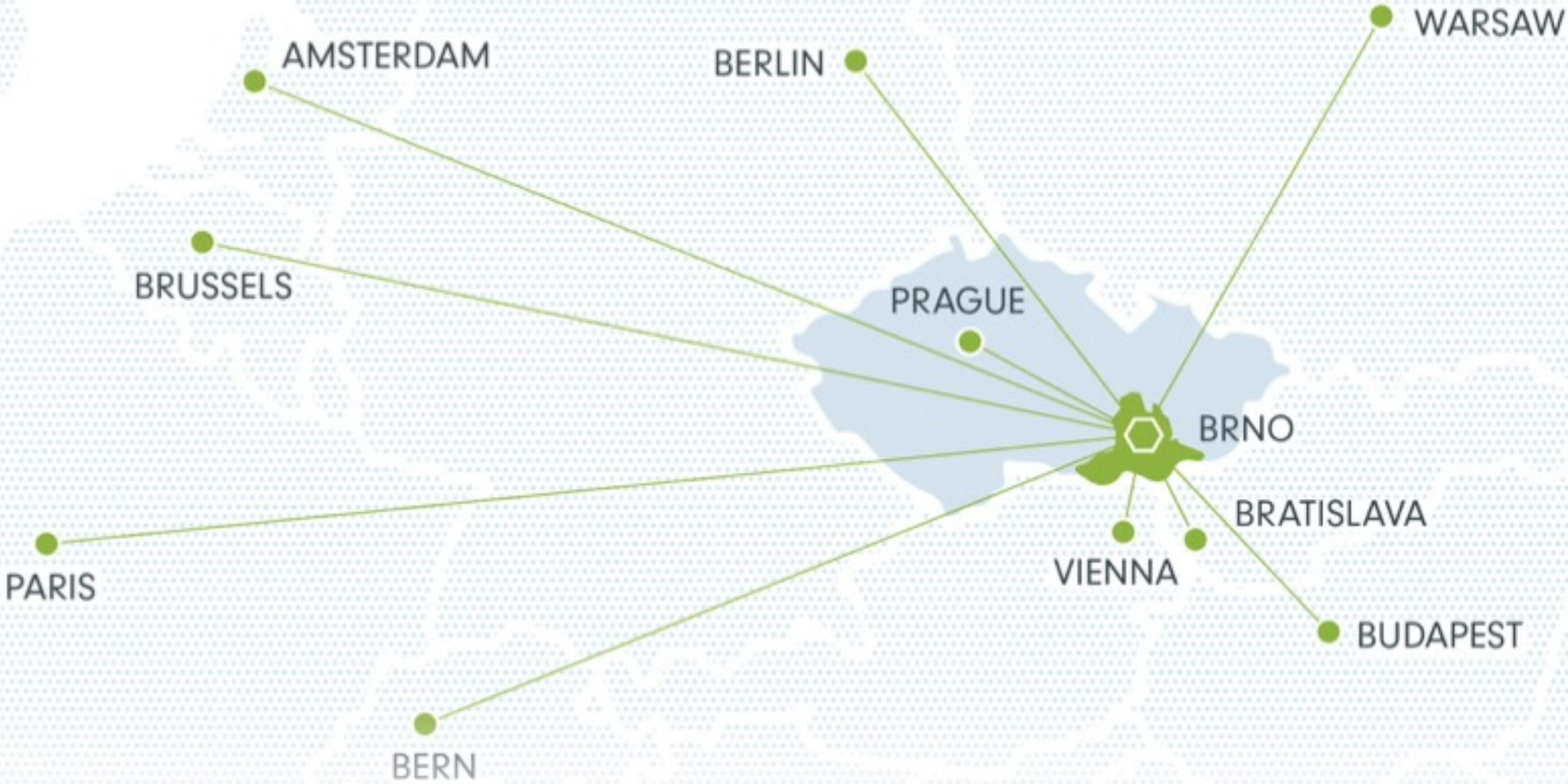
Outline

- State-of-the-art LIBS
  - theory and motivation
  - limitations and challenges
  - instrumentation development
- Application driven research
  - needs for polymer analysis
  - LIBS in polymer recycling
  - calibrating the LIBS Scout
- Conclusion

IFATI4-2021

International Forum

Advanced Technology for Industry 4.0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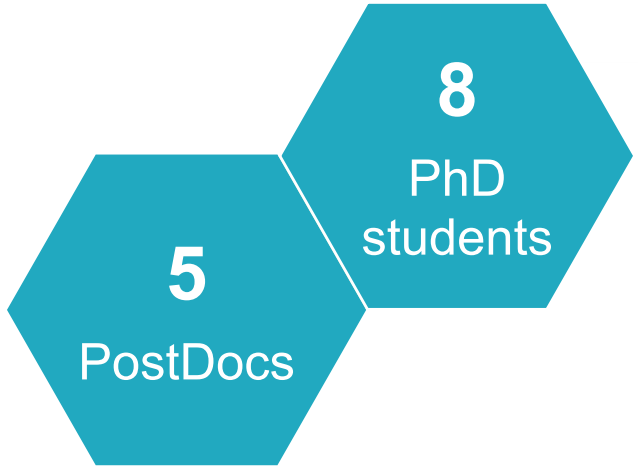
RG1-6: Advanced Instrumentations and Methods for Materials Characterization

- Main objectives – **react to recent trends and R&D activities in a broad range of scientific fields worldwide** including aerospace, automotive, power generation industry, biology and electronics.
- Research Group Leader – **Prof. Jozef Kaiser**
- **32** Researchers / **30** PhD students (42.8 FTE)
- **2** Research lines
  - Computed Tomography
  - Laser Spectroscopy

Laser Spectroscopy laboratory

- Head of the Research Line – **Dr. Pavel Pořízka**
- Our vision is to **transfer high-end science to daily routine**.
- Our mission is
  - **to bridge the gap between technical and bio-sciences**,
  - to develop **state-of-the-art instrumentation** and
  - toprovide **professional analytical services**.



State-of-the-art LIBS

Theory and motivation
Limitations and challenges
Instrumentation development

Laser-Induced Breakdown Spectroscopy

in *stand-off*, large-scale, and high-throughput analysis

benefits

- large scale mapping
- micro-scale resolution
- real-time response
- multielemental
  incl. C, H and light elements (Na, Li, Mg)
- high **sensitivity**
  (ppm ≈ µg/g level)
- depth profiling

applications

- bio-research and toxicology
- geology and agriculture
- automotive and industry
- polymer production

LIBS and other techniques of analytical chemistry

Advantages and drawbacks

analytical technique	sample		instrumentation		analytical performance		
	preparation	throughput	stand-off	handheld	sensitivity	stability	carbon
LIBS	none	high	yes	yes	ppm	medium	yes
X-Ray Fluorescence	none	high	no	yes	ppm	medium	no
Spark Discharge-OES	none	medium	no	yes	ppb	low	yes
Flame AAS	extensive	low	no	no	ppb	high	yes
ICP-OES/MS	extensive	low	no	no	ppt	high	yes

References: thermofisher.com and chem.libretexts.org

Laser-ablation assisted spark discharge optical emission spectroscopy

S. Grünberger et al. *Optics & Laser Technology* **123**, 2020, 105944. j.optlastec.2019.105944

S. Grünberger et al. *Spectrochimica Acta Part B* **169**, 2020, 105884. j.sab.2020.105884

LIBS instrumentation for Industry 4.0

Instrumental challanges

- Real-time and *in-situ* analysis
- Robust system
  - *stand-off* or
  - handheld/remote
- Affordability: cost-to-performance ratio

Case study: LIBS for firing ceramics

BEST MORAVITCARBO

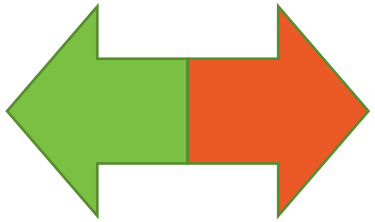
LIGHTIGO
LIGHT UP YOUR ANALYSIS

BB-1 LIBS system

- 1 – 3 meters stand-off
- harsh environments
- double pulse LIBS

Instrumentation development

Transfer of technology



Plastics Cluster

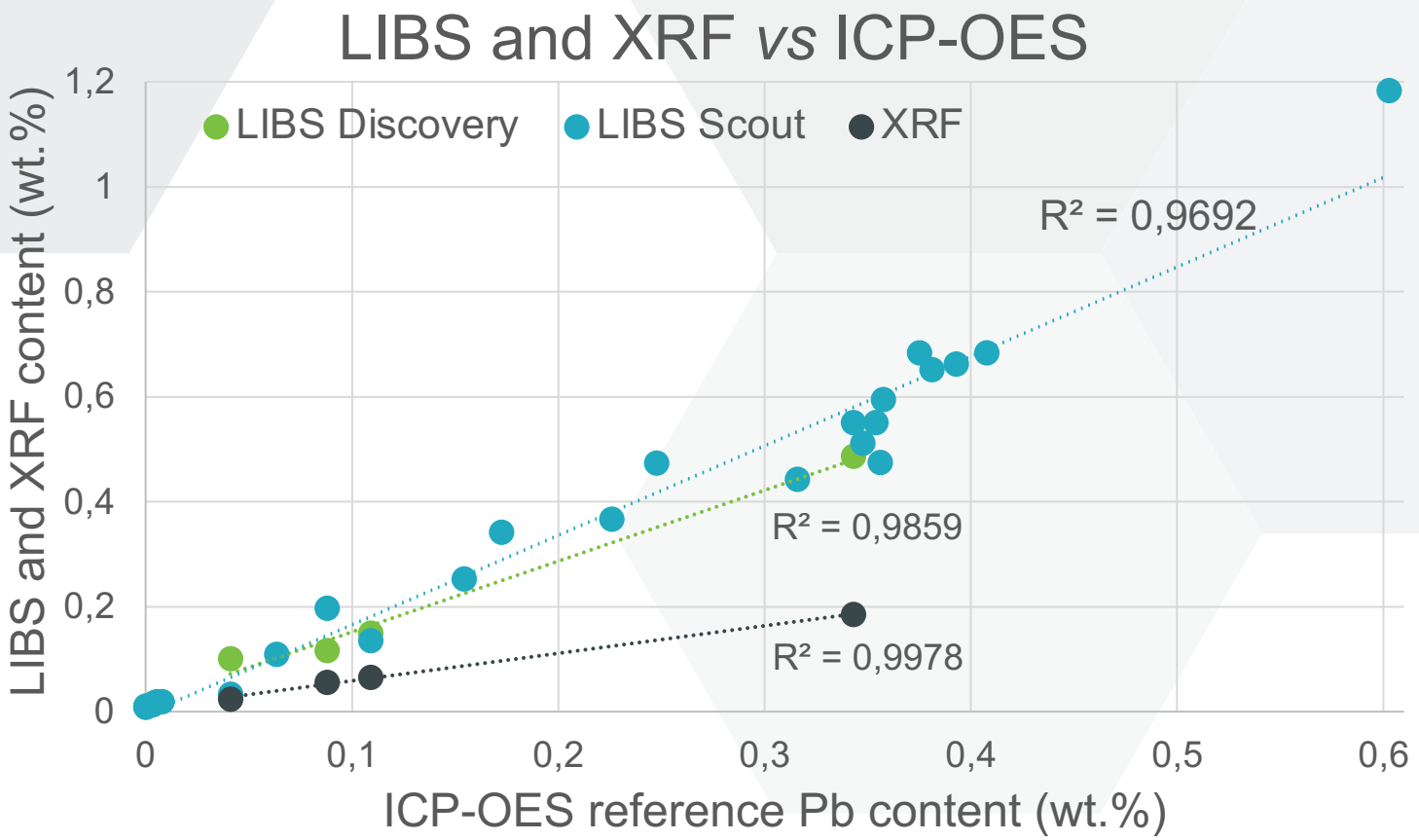
LIBS Scout

LIBS FireFly

LIBS analysis for the Industry 4.0

Analytical challenges

- Ablation of various matrix (main polymer) and heterogeneous mixtures
- Necessity of matrix-matched standards and external calibration
- Real-time feedback with high accuracy
- Robust calibration model with respect to fluctuation in the analytical performance of a typical LIBS system



Application driven research

Needs for polymer analysis
LIBS in polymer recycling
Calibrating the LIBS Scout

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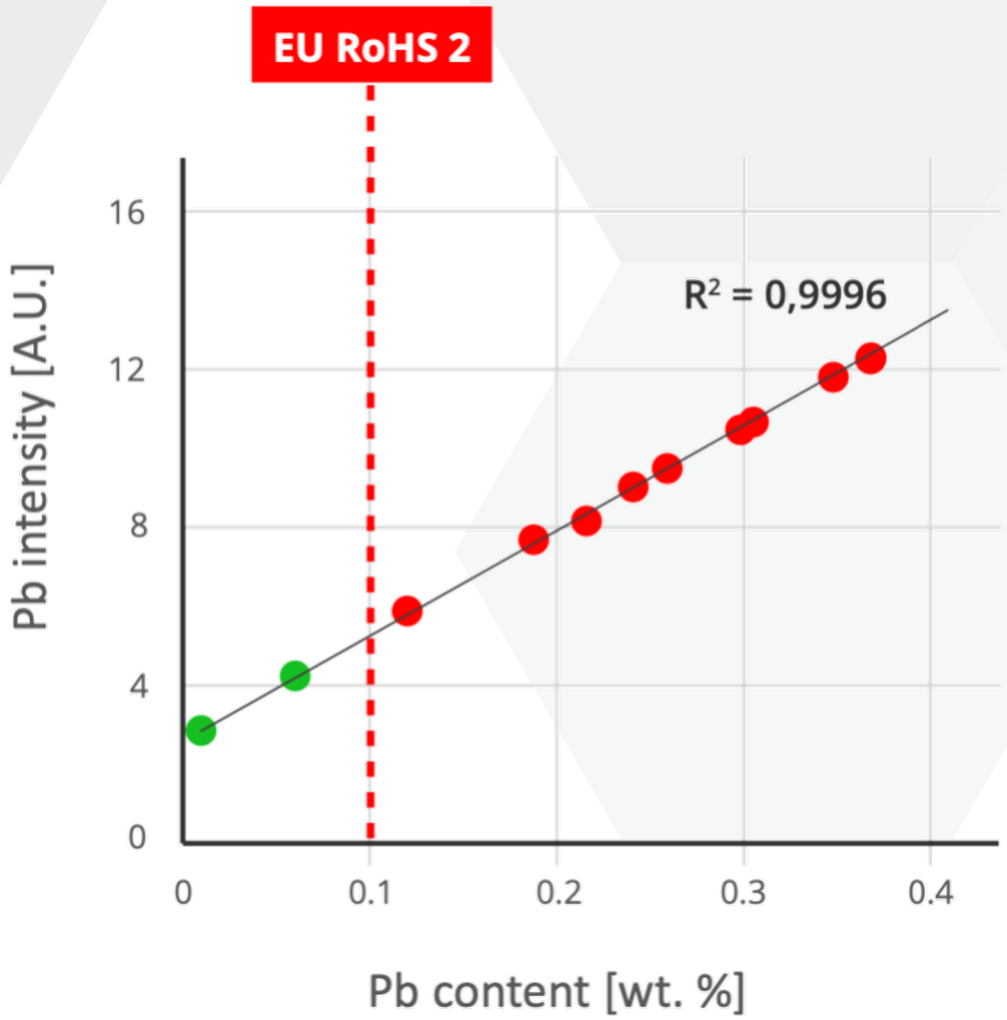
Challenges of polymer analysis

- Limits by EU legislative
  - RoHS, WEEE, and REACH
  - max. content of toxic metals
    - 0,1 wt.% Pb, Hg, and Cr(VI)
    - 0,01 wt.% Cd

- Methodology
  - prediction of Pb in
    - selected for its highest content in polymer matrices
  - LIBS analysis output: OK/NotOK



Polymer ablation

- Laser ablation of polymers
  - detection of C_2 and CN bands
  - varying experimental conditions

Polymer Testing 96 (2021) 107079

Contents lists available at ScienceDirect

Polymer Testing

journal homepage: http://www.elsevier.com/locate/polytest

DOI: 10.1016/j.polymertesting.2021.107079

Laser-Induced Breakdown Spectroscopy analysis of polymers in three different atmospheres

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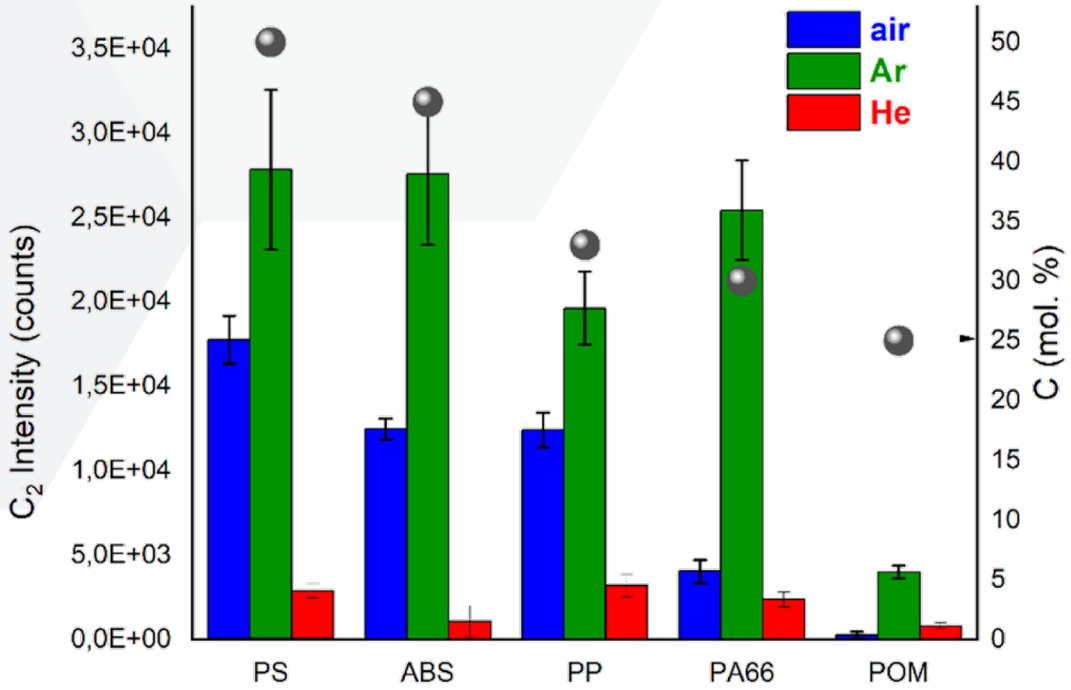
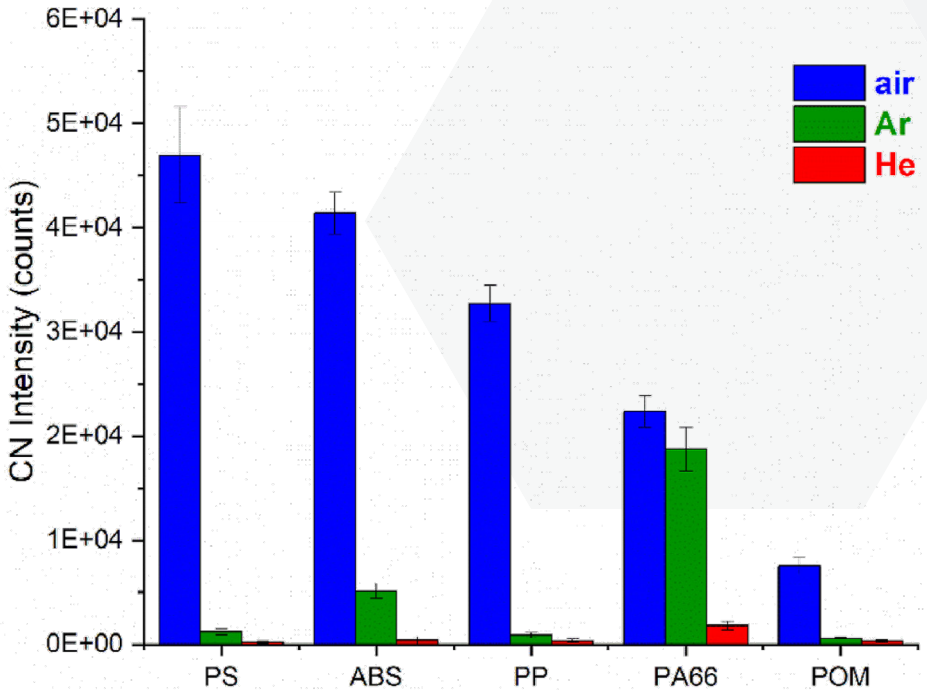
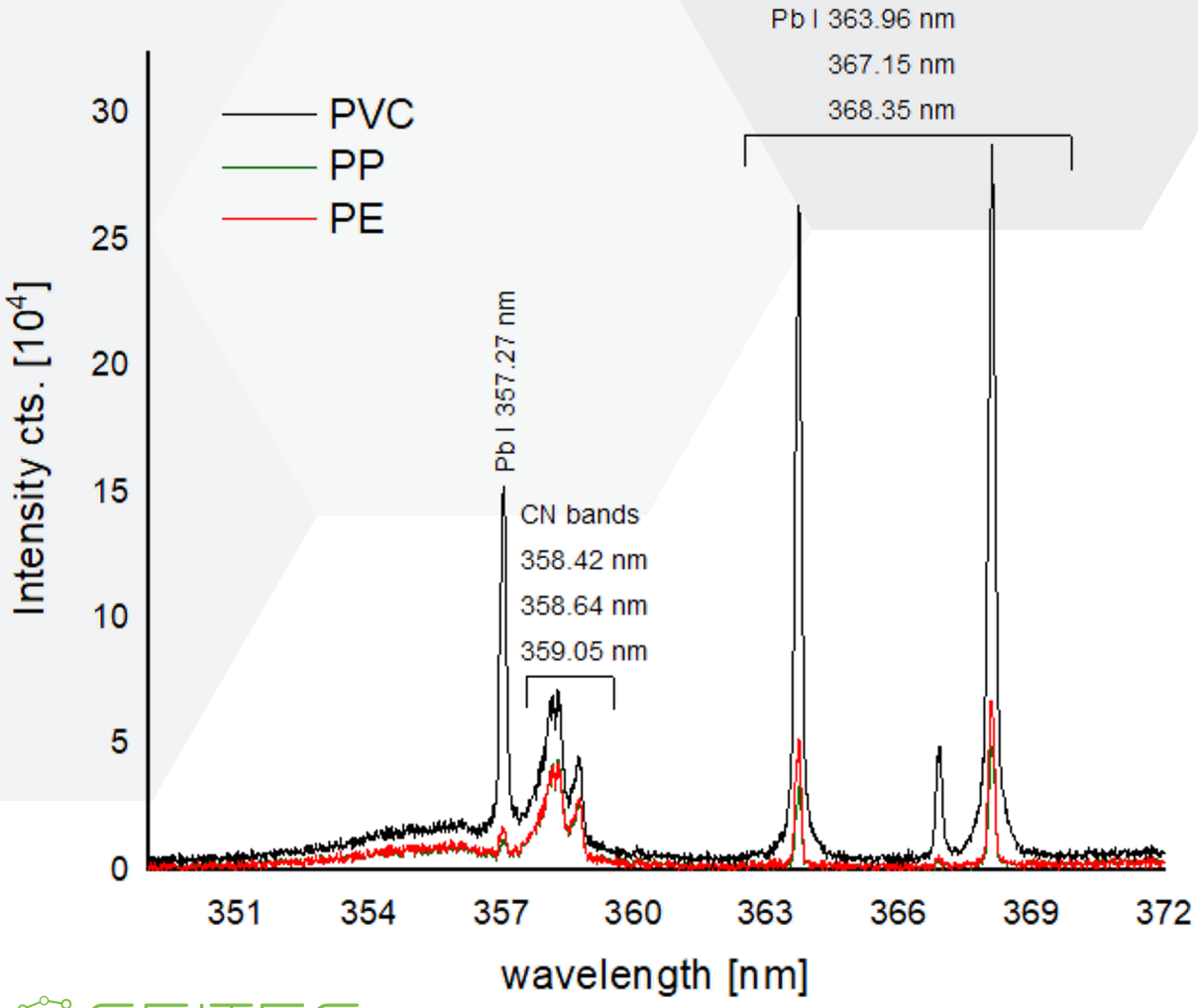
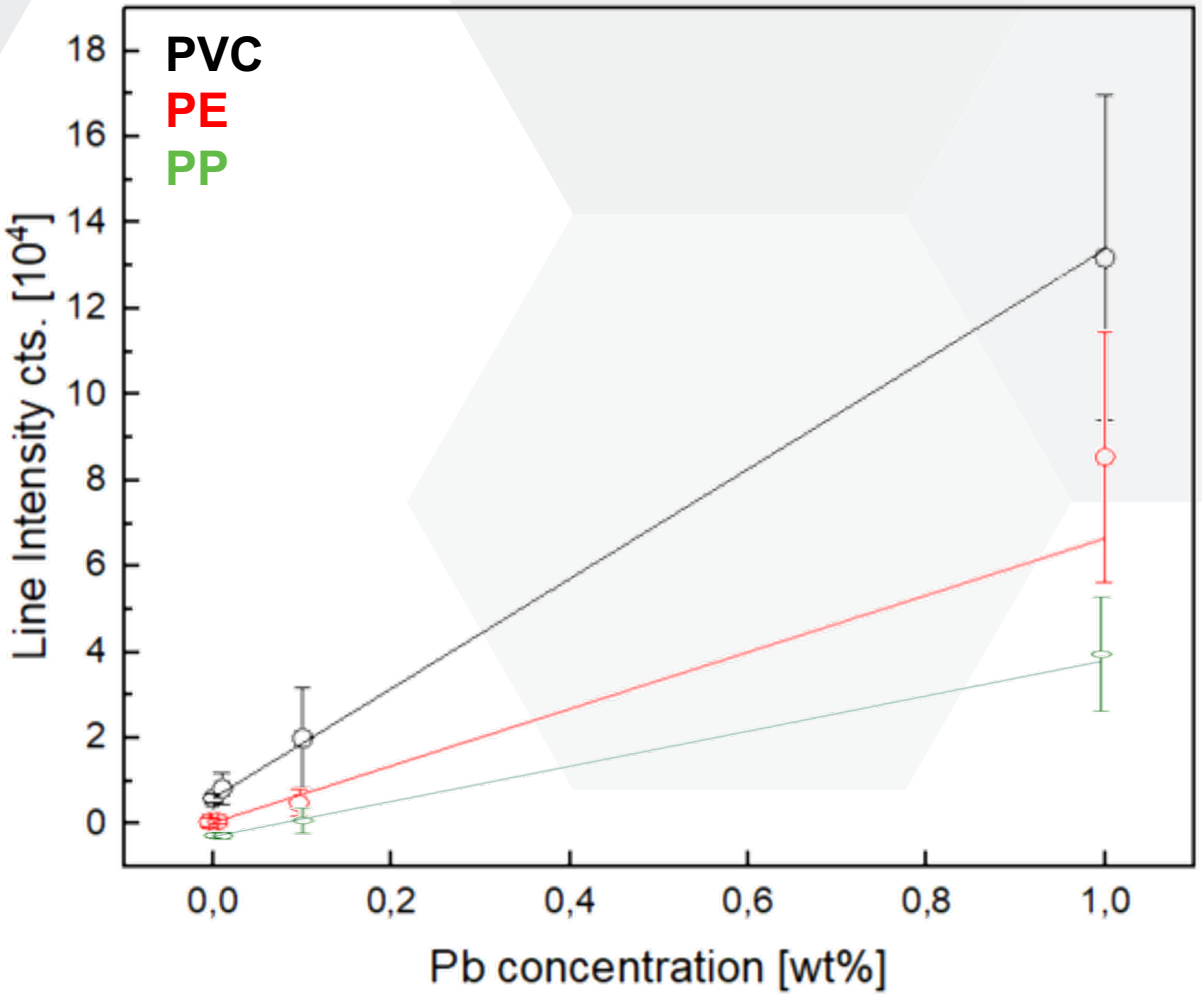




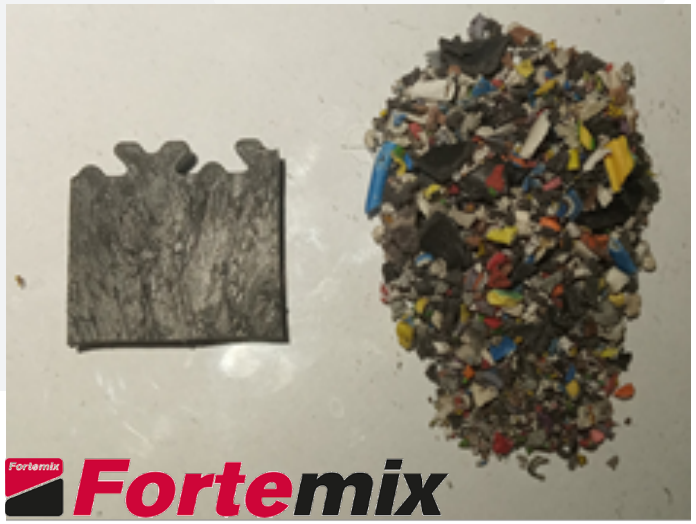
Matrix effect beyond ablation of individual polymers



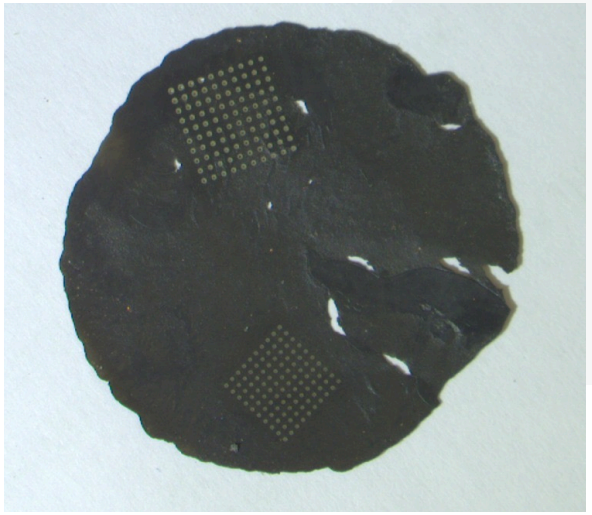


LIBS in polymer recycling

real samples from polymer production, recycling of post-consumer eWaste



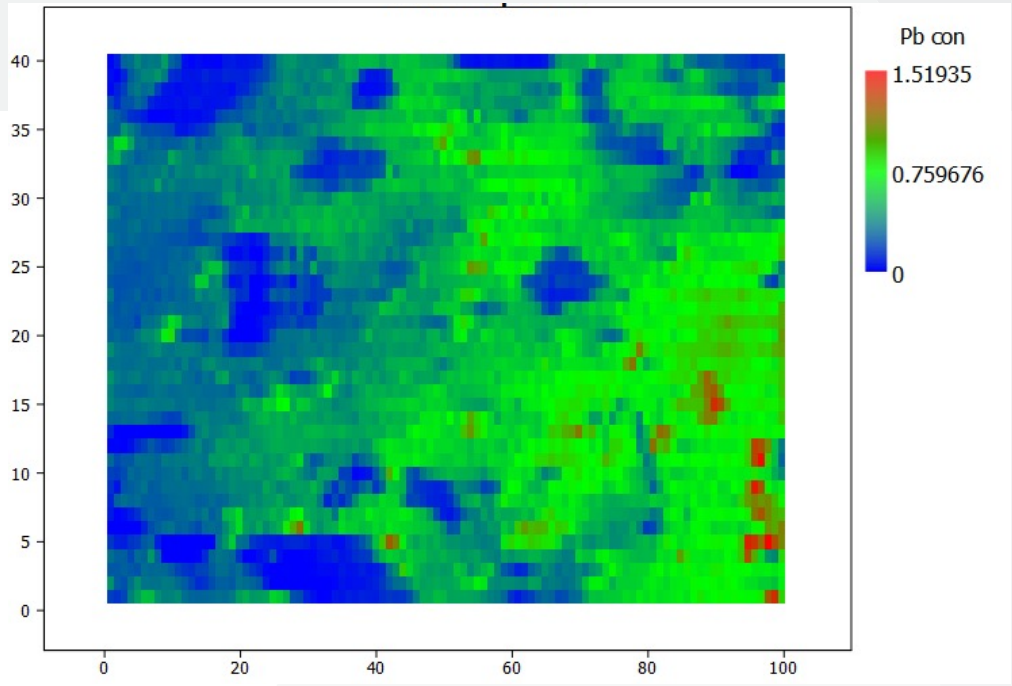
piece of tested product (left) from recycled material (right)

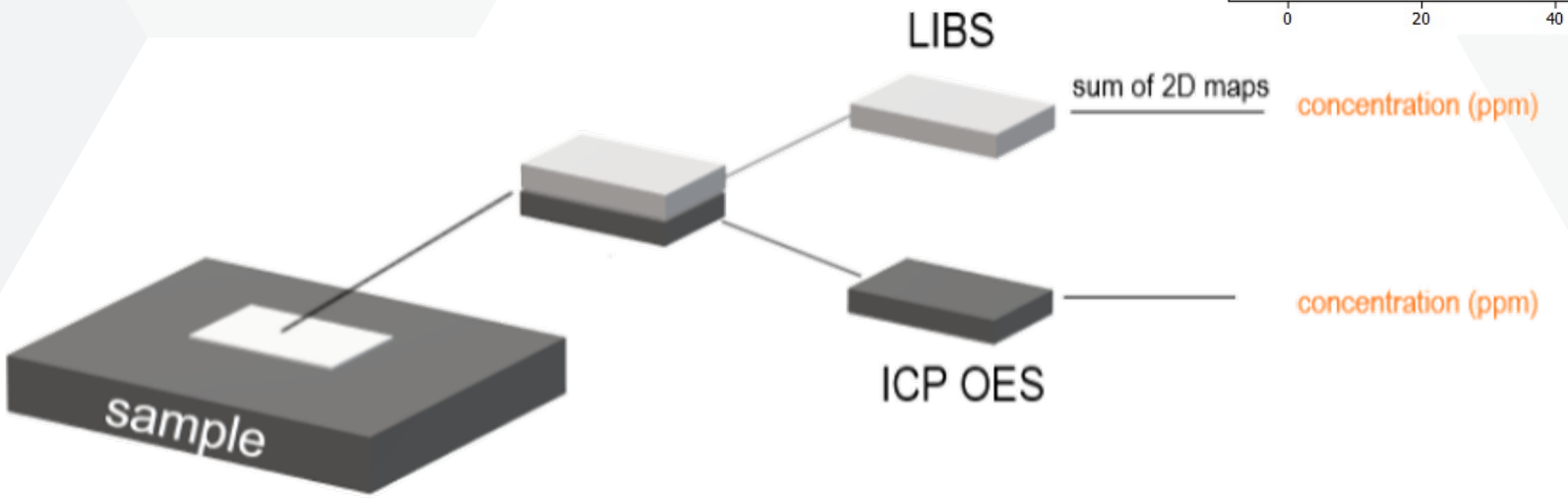


creation of matrix-matched standards and their reference using ICP-OES after acid digestion

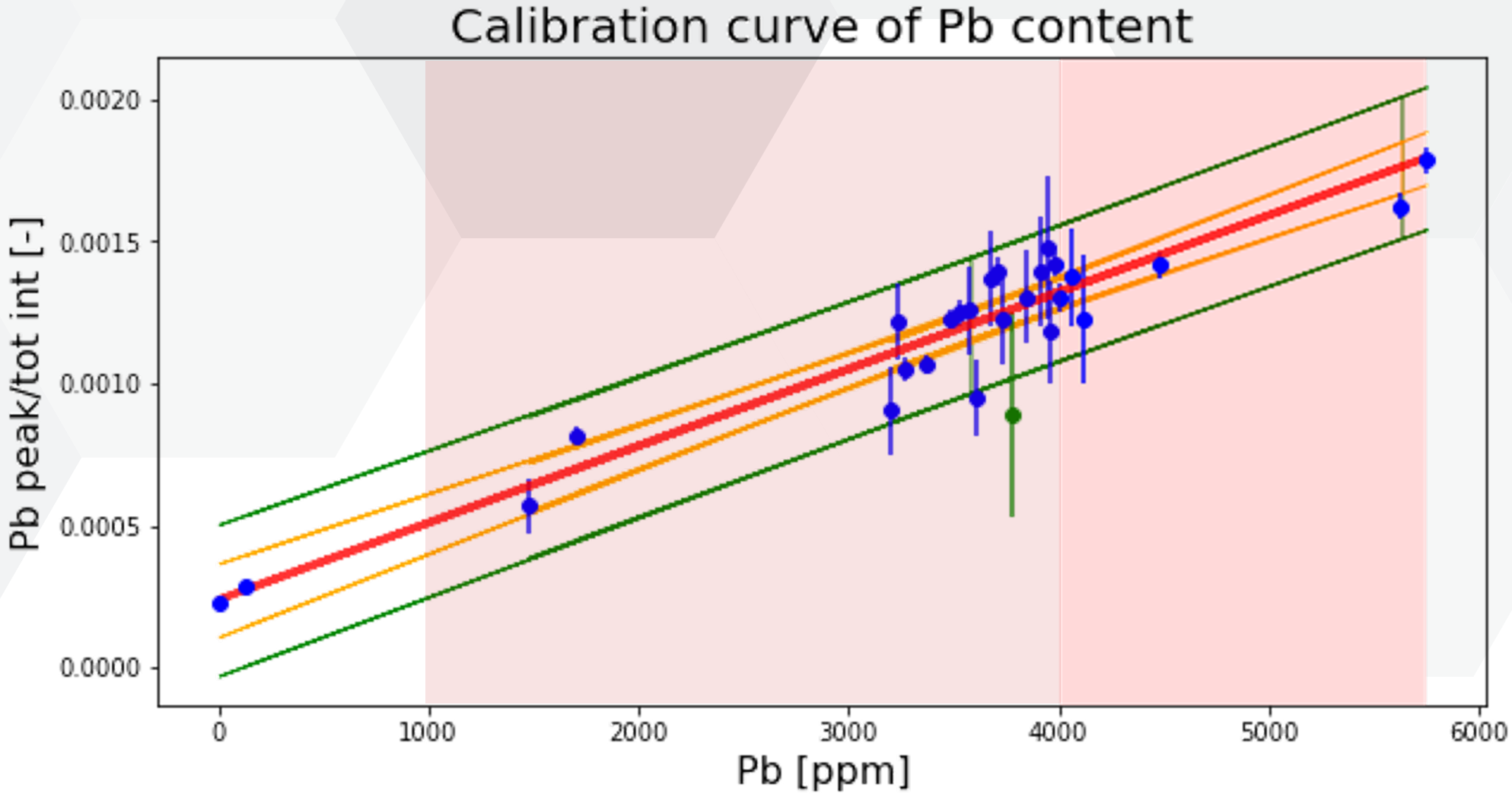
LIBS in polymer recycling

- From LIBS analysis (Pb intensity image) to Pb content
- Creating calibration standards
- Optimizing ablation conditions and data processing





LIBS in polymer recycling



Conclusion

Ongoing and future work

- Improvements in instrumentation
  - stand-off detection with real-time feedback to production
  - robust and durable systems for harsh environments for in-line analysis
  - optimizing the trade-off between analytical performance and system+analysis costs
- Improvements in sample analysis and data processing
  - higher accuracy and trueness through high number of LIBS spectra
  - implementation of machine learning algorithms
    - to mitigate matrix effects
    - mitigation of spectral interferences and non-linearities
  - **transfer learning – data library transfer between individual LIBS systems**
    - **transfer through non-linear algorithms**

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Cooperation

Contacts

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LABORATORY
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WHAT IS LIBS?
FOCUS OF THE LABORATORY
INTERDISCIPLINARY R&D TEAM is engaged in:
LASER SPECTROSCOPY
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