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ENRICH

Universitat de Girona

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X-Ray Fluorescence-Based Methods: An Overview of Applications, Current Challenges, and Opportunities for Future Developments

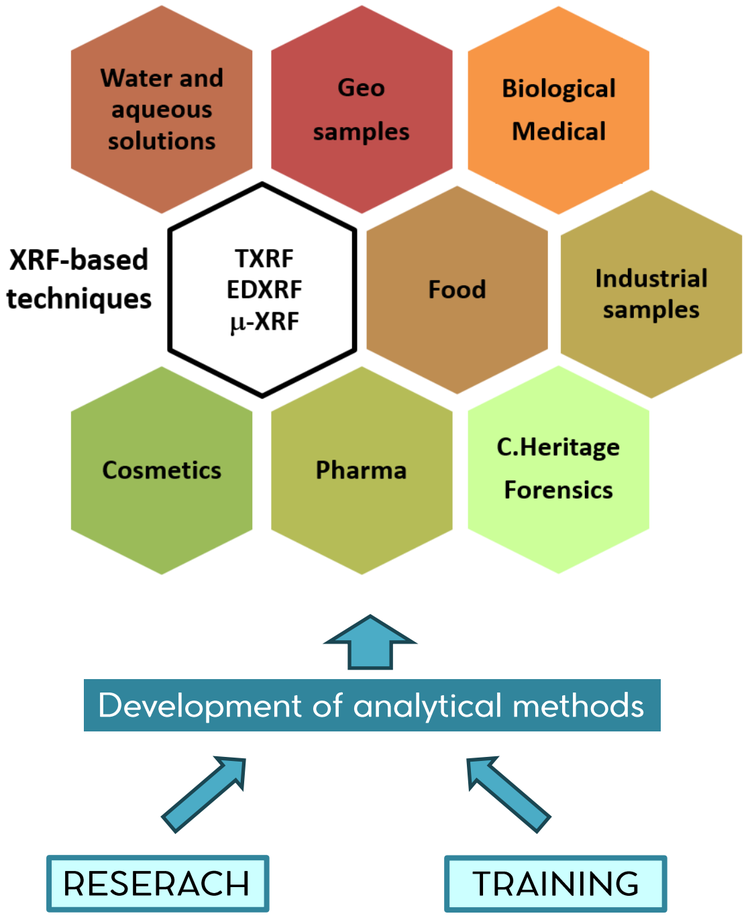
cost EUROPEAN COOPERATION IN SCIENCE & TECHNOLOGY

Funded by the European Union

1st Annual Meeting ENRICH
University of Kraków (Poland), 14-16 July 2026

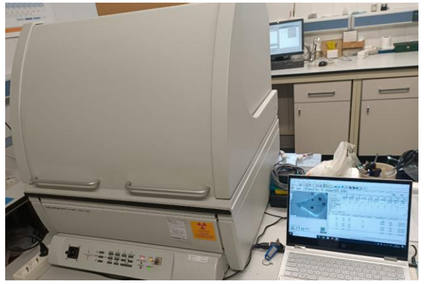
Our research and facilities

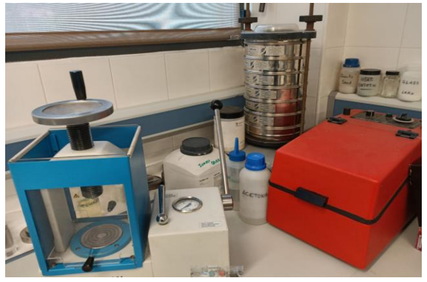
LABORATORY OF X-RAY FLUORESCENCE APPLICATIONS (LARX)



- Available instrumentation:
  - EDXRF: S2 Ranger, Bruker
  - TXRF: S2 PICOFOX, Bruker
  - μ-XRF: Fischerscope, Helmut-Fischer
  - ICP-OES: 5100 Agilent
  - ICP-MS: 7500c Agilent
- Other equipment:
  - MW oven (Teflon/Quartz reactors)
  - Block heater
  - Incubator
  - Mills
  - Preparation of pressed pellets
  - Shakers (rotatory, orbital…)
  - (…)

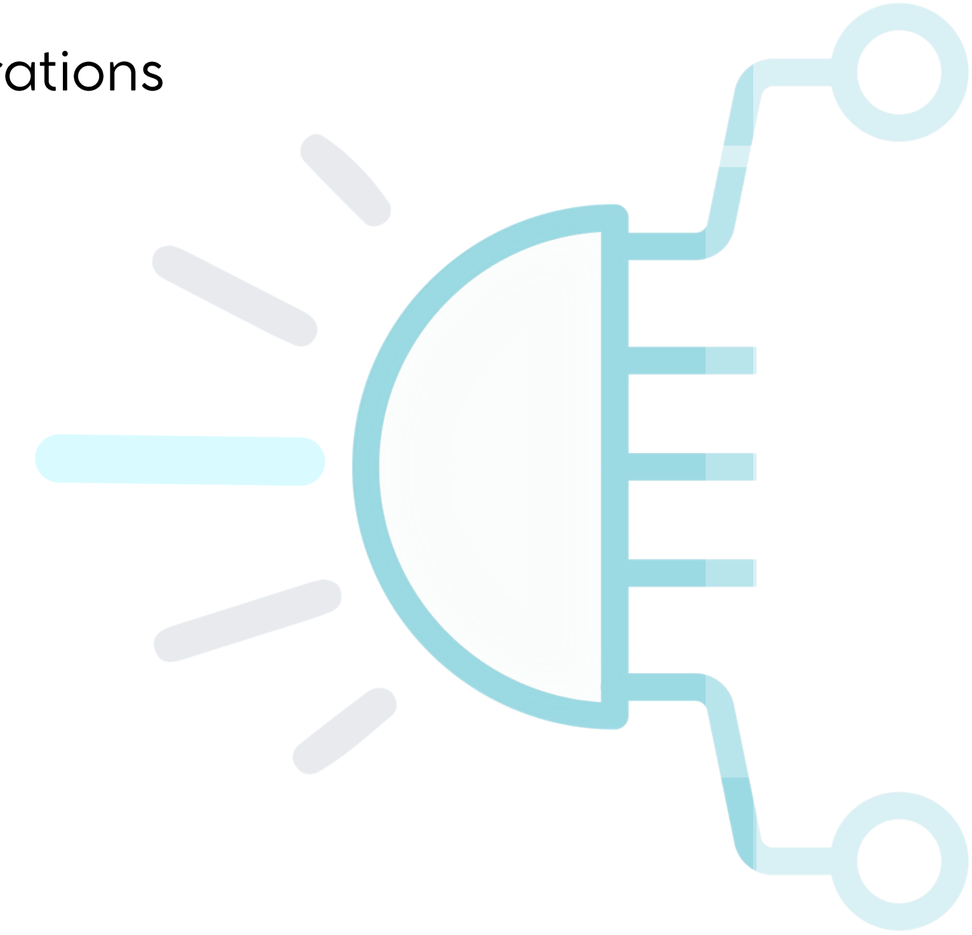
Commercial systems





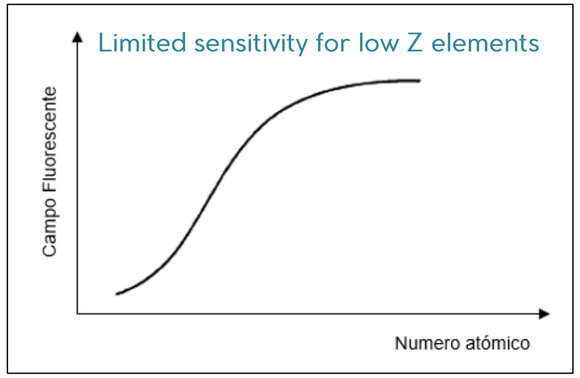
Outline of the presentation

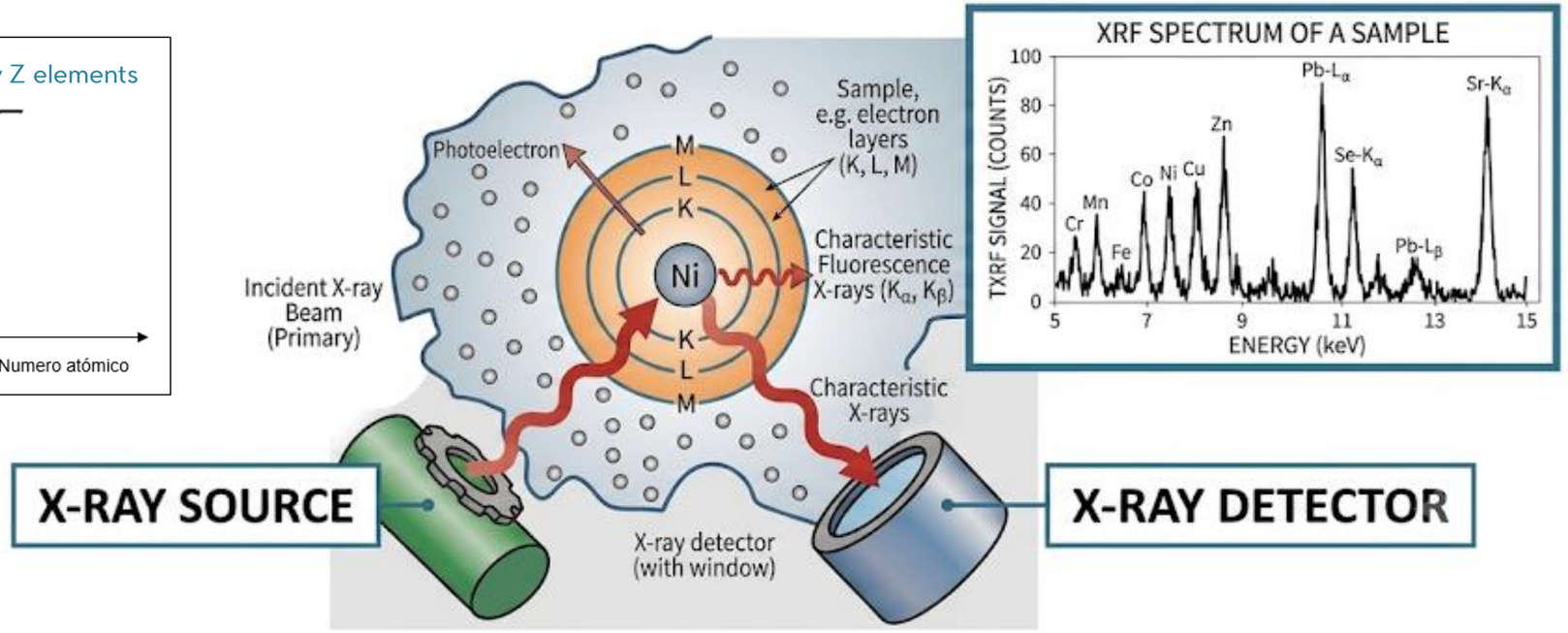
- Basic principles of XRF and instrumental configurations
- Role of XRF in the analtyical chemistry field
- Critical stages and examples of XRF applications
- Future perspectives and Challenges
- Concluding remarks
- Acknowledgments



Basic principles of XRF and instrumental configurations

The atoms in the sample are excited and emit characteristic X-rays





Energy of the characteristic X-rays → Elements present in the sample (Qualitative)

Numer of photons of each element → Element concentration (Quantitative)

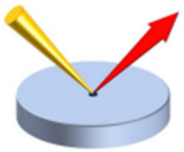
Commercial EDXRF systems

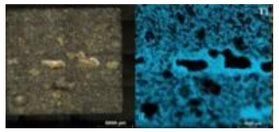
EDXRF
Energy dispersive XRF

- Mostly benchtop systems (50W)
- Mostly analysis of solid samples
- Bulk analysis (macro)
- Simultaneous multielemental capability
- Screening information
- Major, minor, trace elements

µ-XRF
Micro XRF

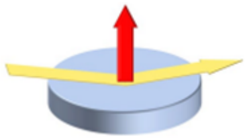
- Local analysis
- Elemental mappings





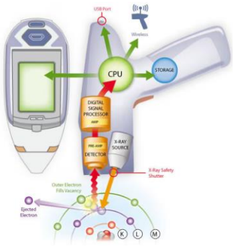
TXRF
Total Reflection XRF

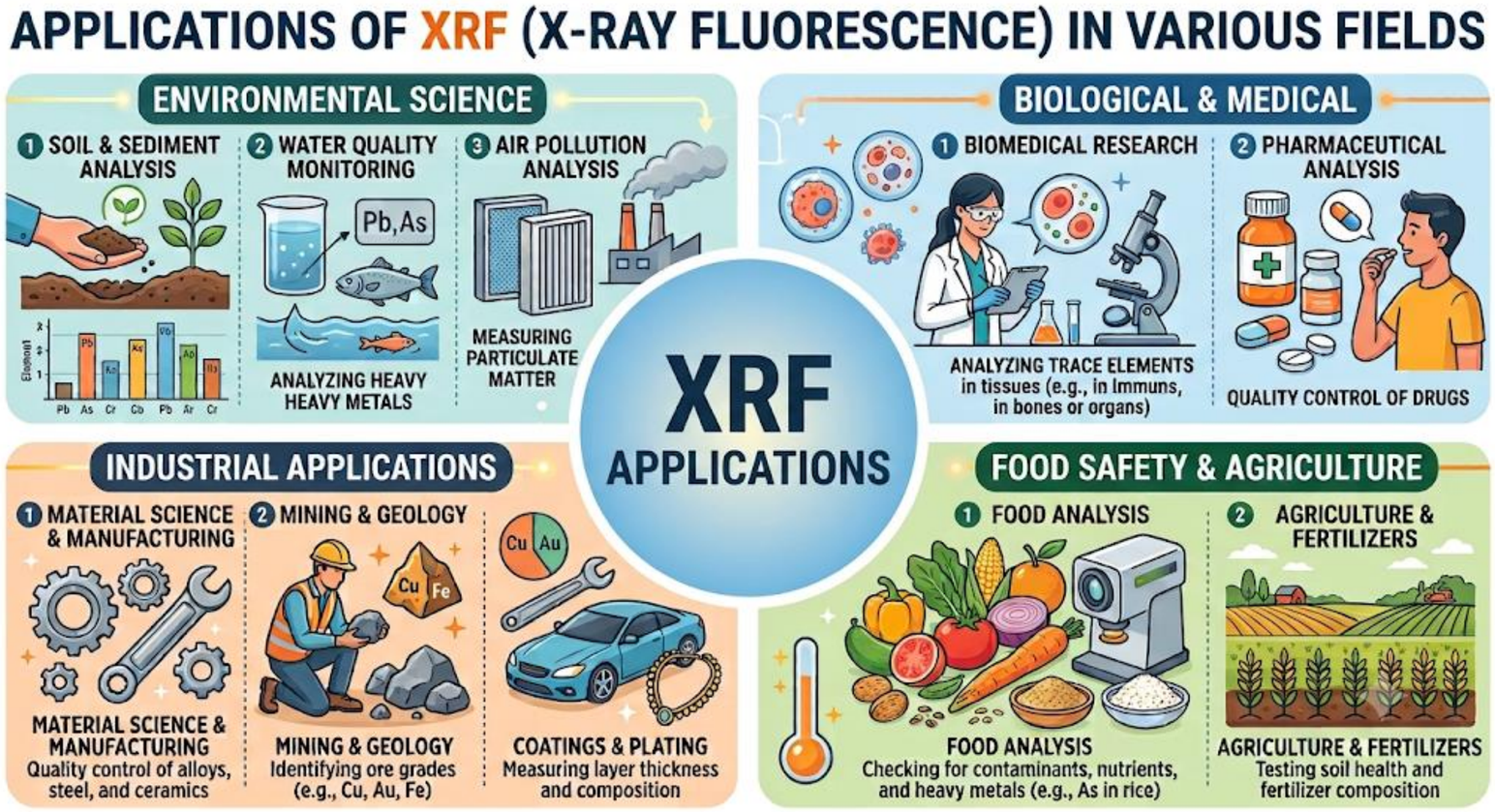
- Bulk analysis (micro)
- Improved sensitivity (traces)
- Liquid sample analysis
- Easy quantification (Internal Standard)



p-XRF
Portable XRF

- In-situ analysis





General requirements for analytical methods

- ✓ Obtain realiable data on element content
- ✓ Enable end-users to make informed decisions and to address the problems effectively.
- ✓ High trouhput, fast, low-cost
- ✓ Alignment with principles of green analytical chemistry (**GAC**)

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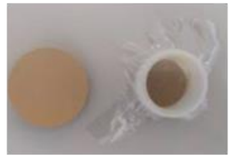
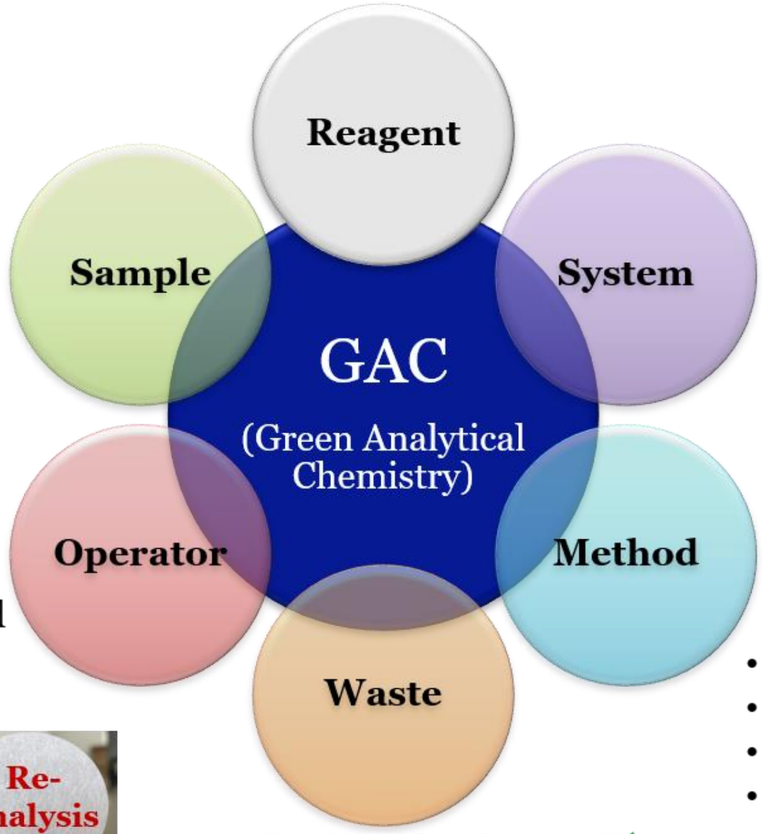
Role of XRF in the analtyical chemistry field

- **Reduction of reagents** ☑
- **Non-toxic, safe** ☑
- From renewable source



- Minimal number
- ☑ **Minimal size**

- ☑ Safety ensured



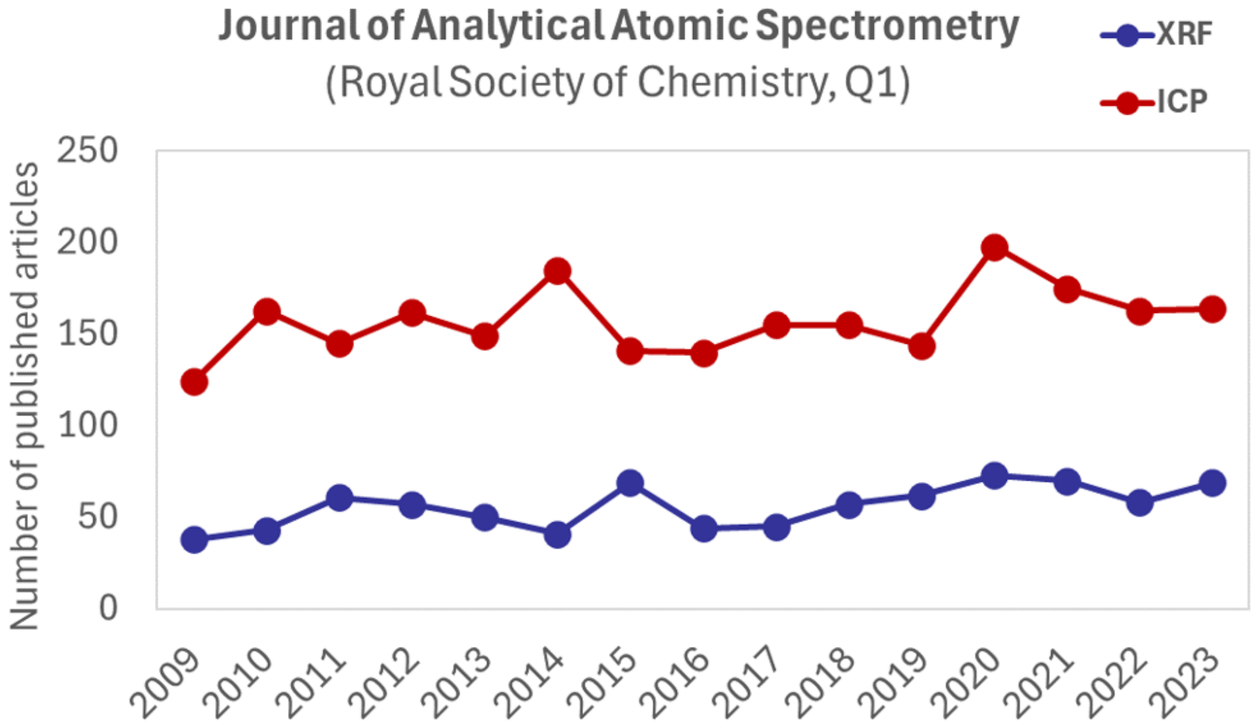
- **Reduced volume** ☑
- Properly treated

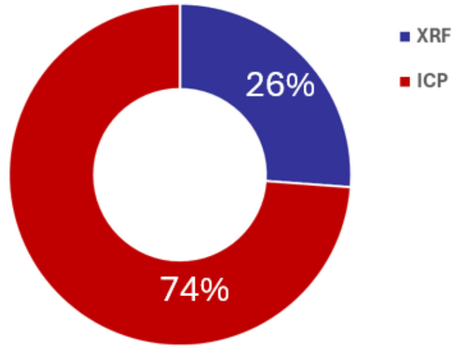
- **Energy efficient** ☑
- **Miniaturized** ☑
- **Multiparametric** ☑

- **Automated, in-situ** ☑
- **No sample treatment** ☑
- **No derivatization** ☑
- Processes and operations integrated

Role of XRF in the analtyical chemistry field

Publication of scientific articles in Spectroscopic Journals (2009-2023, last 15 years)





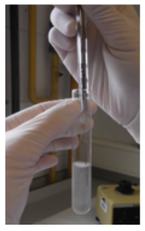
Critical stages and examples of XRF applications

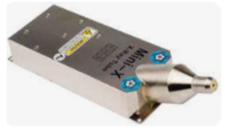
Sample preparation

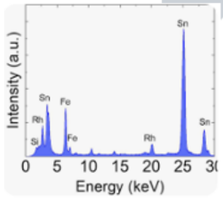
Hardware

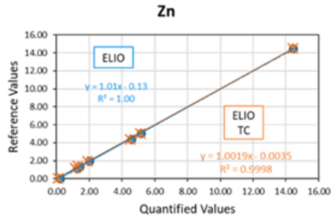
Quantification

XRF results



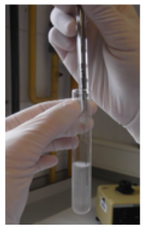


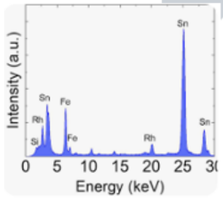


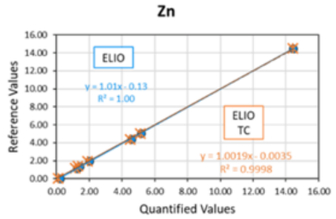


Critical stages and examples of XRF applications

Sample preparation → Hardware → Quantification → **XRF results**





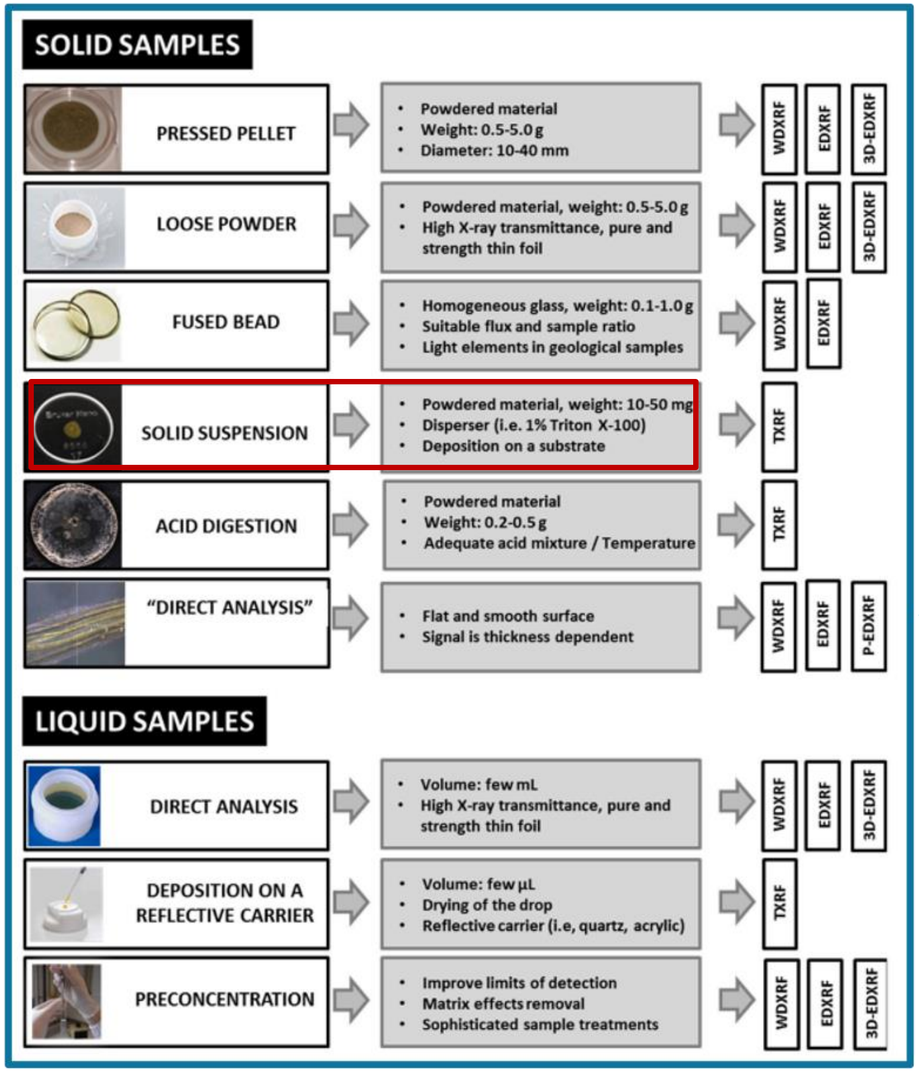


Critical stages and examples of XRF applications

Sample Preparation

Simple sample treatment of solid samples

Limited applications to liquid sample analysis

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Eva Marguí, Ignasi Queralt

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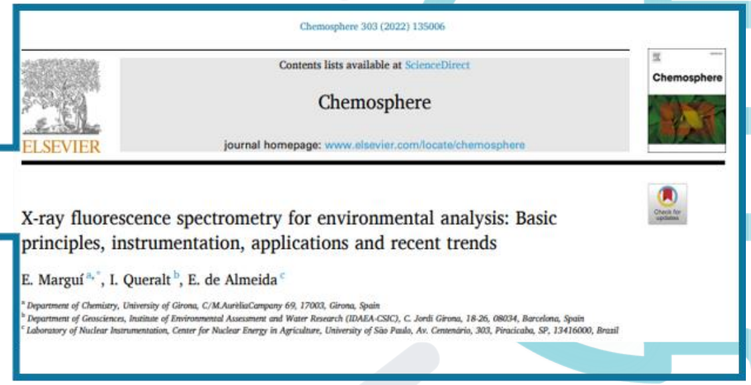
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ELSEVIER

X-ray fluorescence spectrometry for environmental analysis: Basic principles, instrumentation, applications and recent trends

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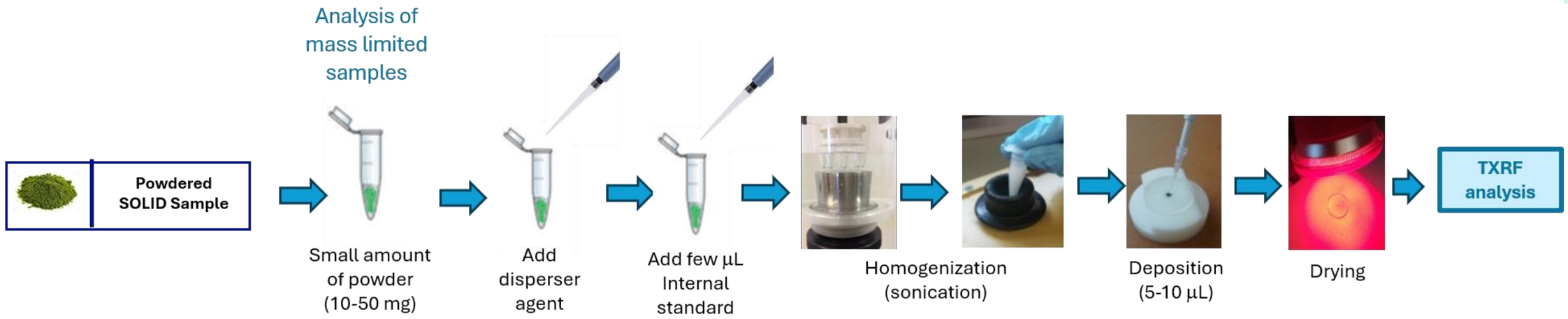
Analysis of solid suspensions by TXRF

Analysis of mass limited samples



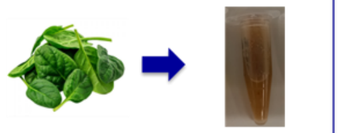
Simple sample treatment! (GAC principles)

GREEN ANALYTICAL CHEMISTRY

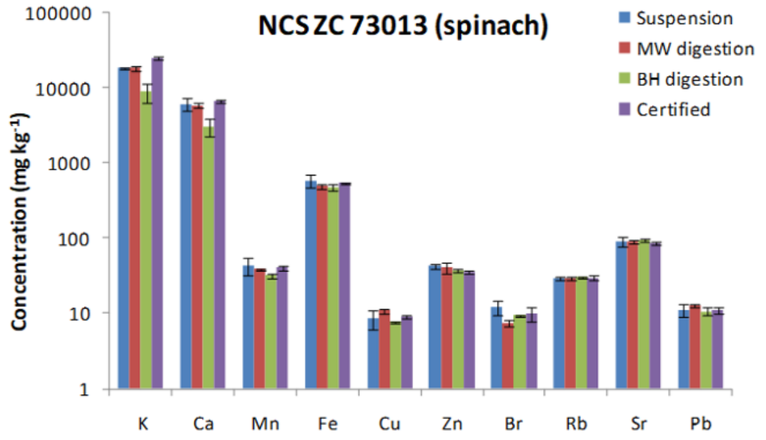
Study in detail suspension preparation steps and quantification approach used to obtain reliable results!

- Homogeneous solid sample (few mg)
- Small particle size (~50µm)
- Adequate dispersing agent
- Homogeneous suspension before deposition
- Ensure a thin layer on the reflector

Examples: Analysis of solid suspensions by TXRF



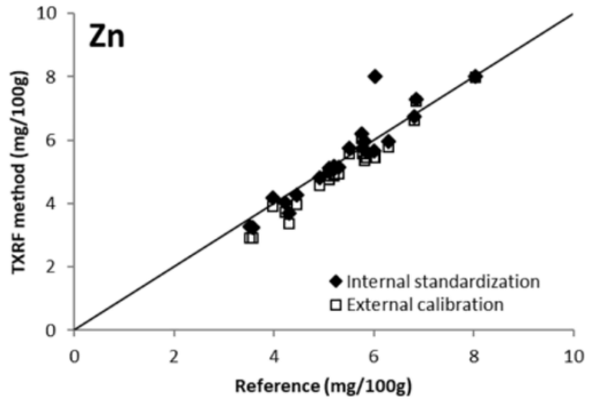
- 20 mg powder milk
- 1 mL MilliQ
- Vortex mixing, 1 min
- 10 µL sample deposition volume



Elemental composition (RM: Spinach leaves) using different samples treatments and TXRF analysis

Dalipi et al. **Food Chemistry 218(2017)348**

- 40 mg powder milk
- 1 mL 1% (v/v) Triton X-100
- Vortex mixing, 1 min
- 10 µL sample deposition volume



Detection limit	P	Cl	K	Ca	Fe	Zn
LD-W (TXRF)	97	45	16.5	4.9	0.4	0.2
LD-Mo (TXRF)	62	3	0.9	0.6	0.1	0.05
Conc. in milk	167 516	295 586	429 1125	255 757	5.1 9.7	3.4 9.5

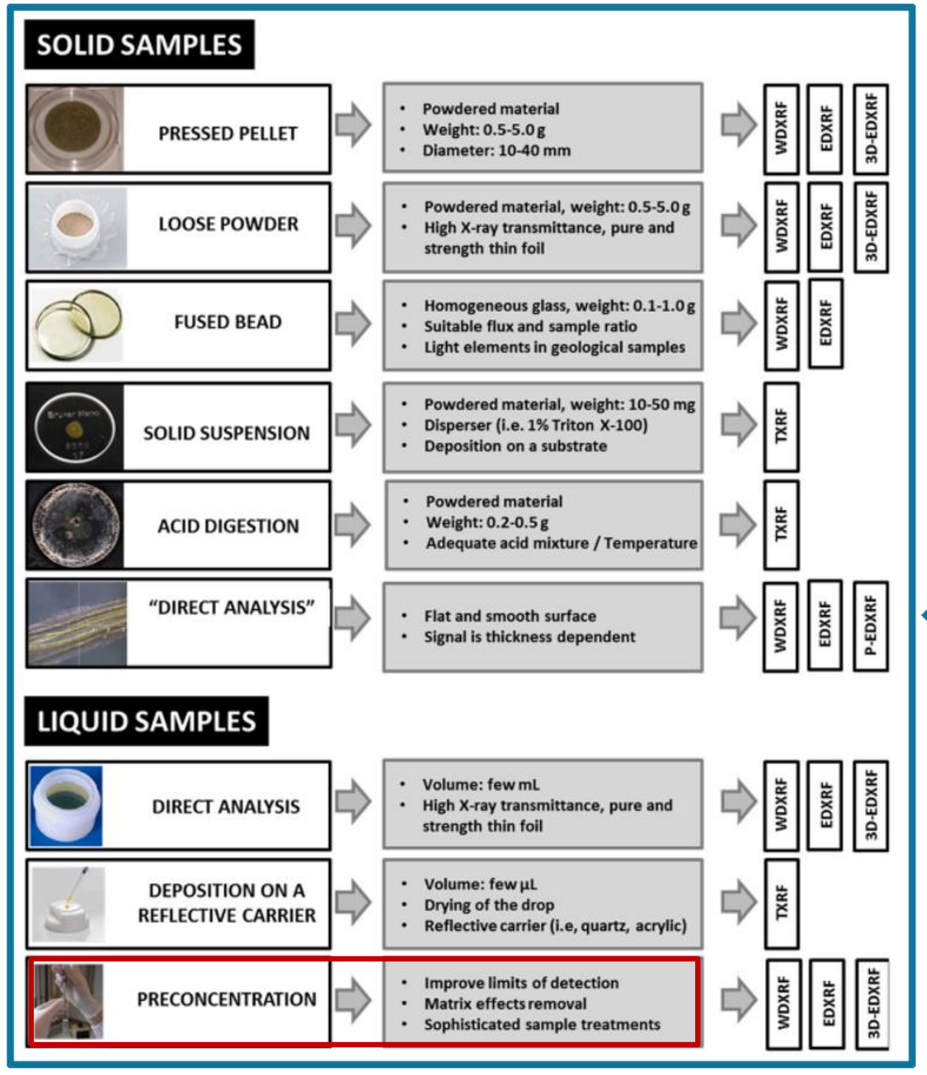
Marguí et al. **Food Chemistry 383(2022)132590**

Critical stages and examples of XRF applications

Sample Preparation

Simple sample treatment of solid samples

Limited applications to liquid sample analysis

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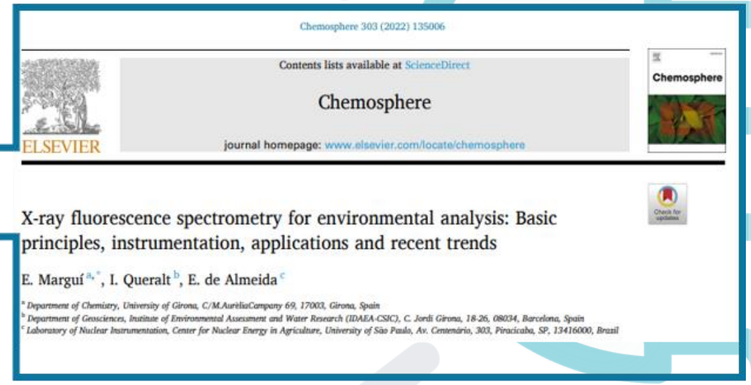
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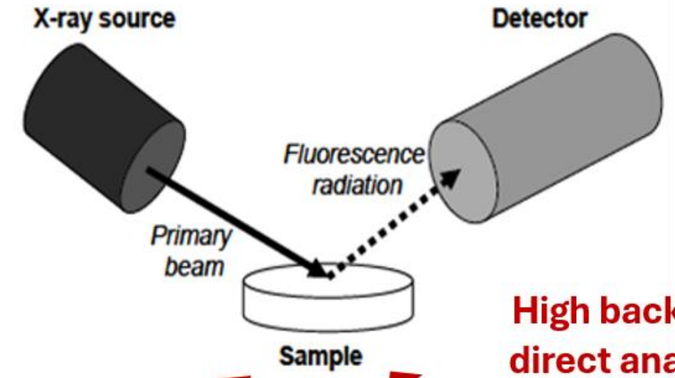
Critical stages and examples of XRF applications

Sample Preparation

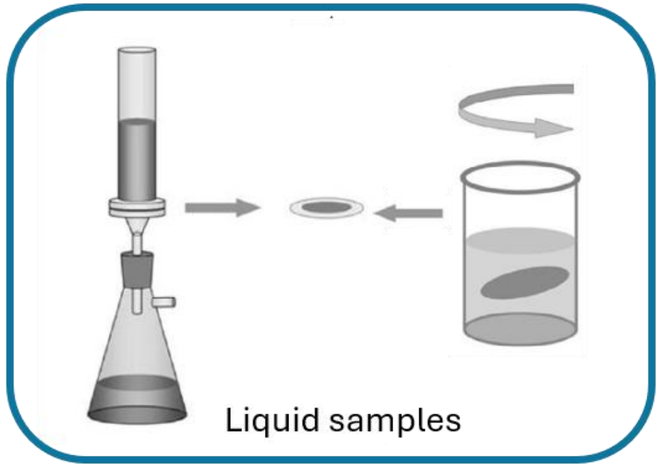
Enhancing the analytical performance of EDXRF for the analysis of liquid samples



High background direct analysis of liquid samples


Solid sample


Liquid sample

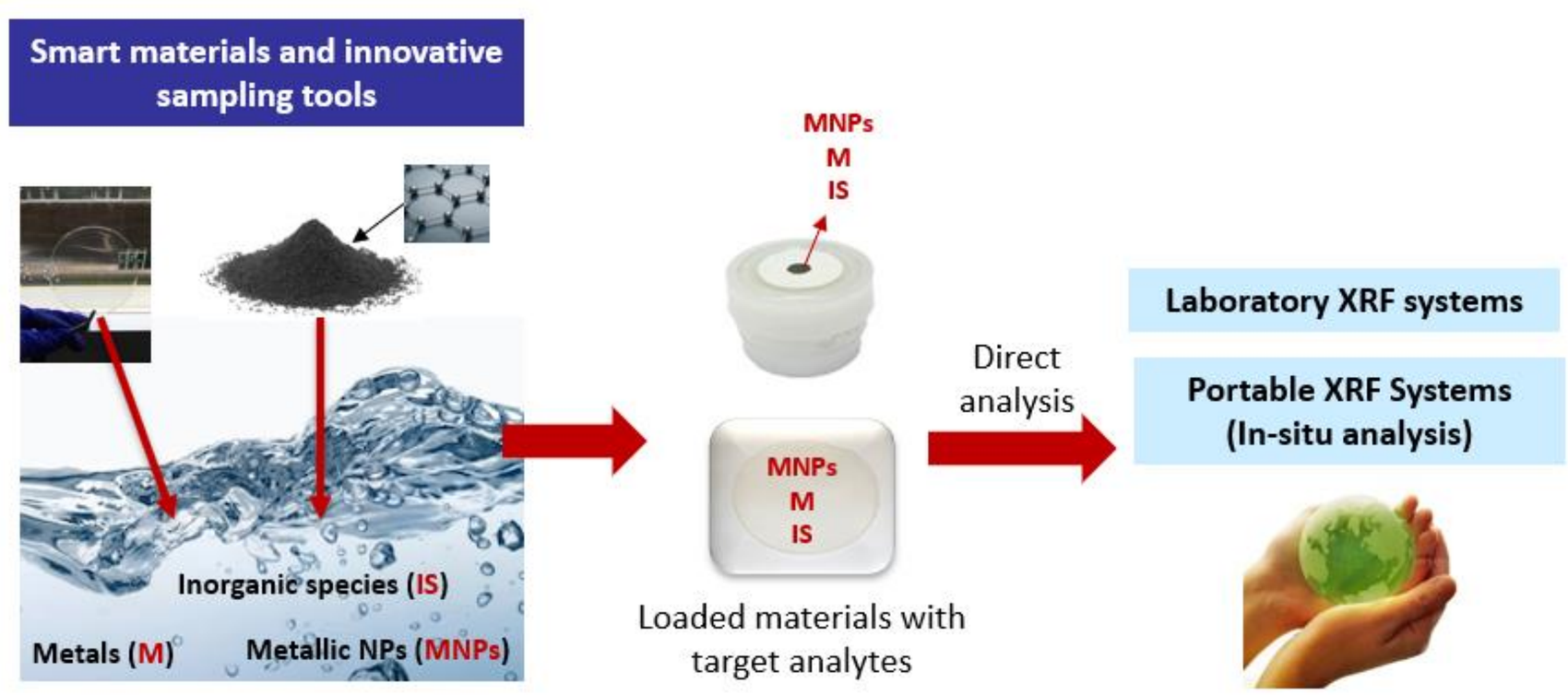


Thin layer organic materials

- ✓ **Directly analyzed by XRF (no elution is needed!)**
- ✓ **Matrix effects are negligible**
- ✓ **Re-analysis**
- ✓ **Better limits of detection**

Sample Preparation

Enhancing the analytical performance of EDXRF for the analysis of liquid samples



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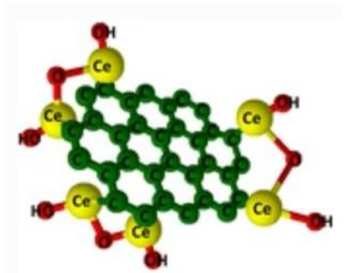
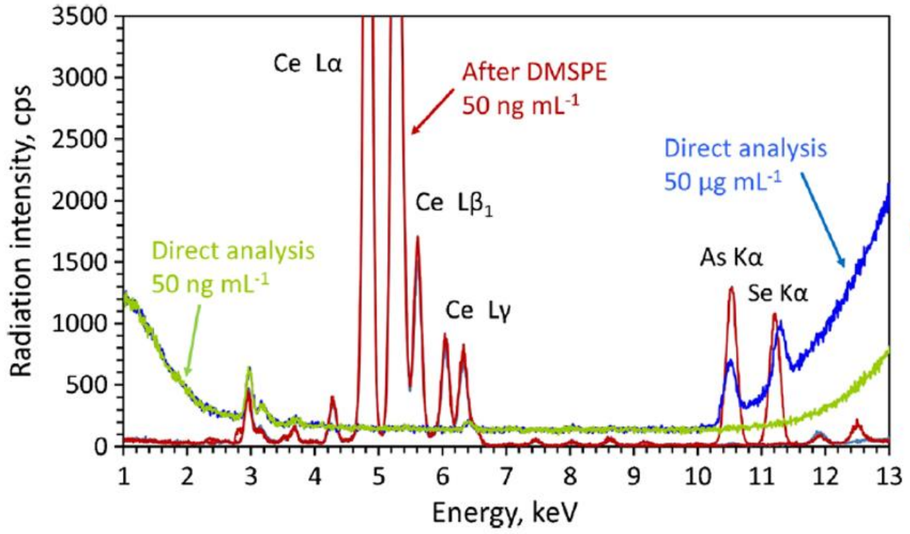
Enhancing the analytical performance of EDXRF for the analysis of liquid samples



Graphene nanosheets and cerium nanoparticles (G/CeO_2)

Use of nanomaterials

- 1 mg nanomaterial
- 25 mL sample
- 5 minutes extraction
- Filtration



Species	Range (ng/mL)	R^2	LD (ng/mL)
As (V)	2.0-50	0.999	0.10
Se (IV)	2.0-50	0.999	0.11
Cu (II)	2.0-50	0.997	0.19
Pb (II)	2.0-50	0.999	0.21

SPECIATION

Marguí et al., **Microchimica Acta 185(2018)264**

Enhancing the analytical performance of EDXRF for the analysis of liquid samples

Chelating disk

Liquid sample

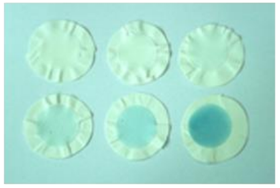
Metals

Chelating disk

Liquid sample

Metals

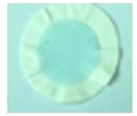
XRF

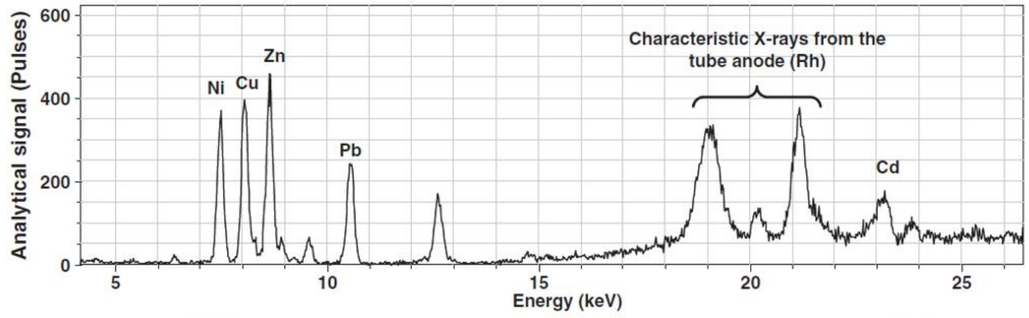


Commercial solid phase chelating disk (3M ™ Empore)

- *Functional group: sodium salt of imminodiacetic acid*

Use of membranes and disks



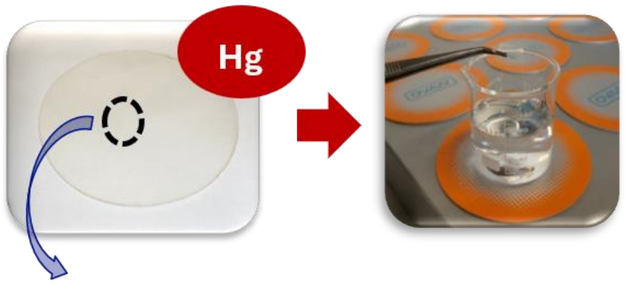


DL	Ni	Cu	Zn	Pb	Cd
µg/L	1.0	1.4	1.1	1.7	7.0

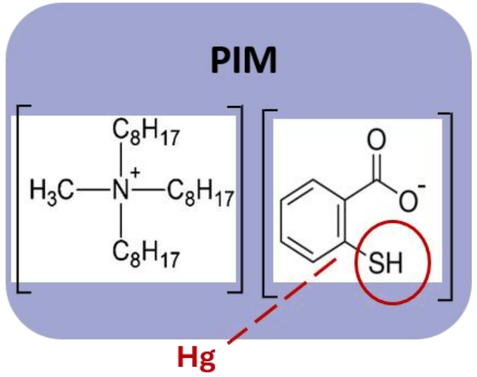
Marguí et al., **Spectrochimica Acta Part B 67(2012)17-23**

Sample Preparation

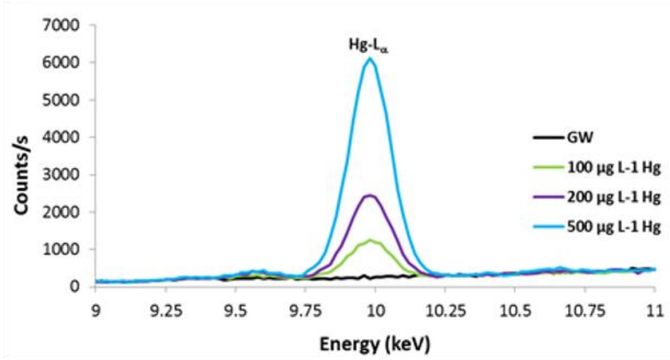
Enhancing the analytical performance of EDXRF for the analysis of liquid samples



50% CTA-50% TOMATS

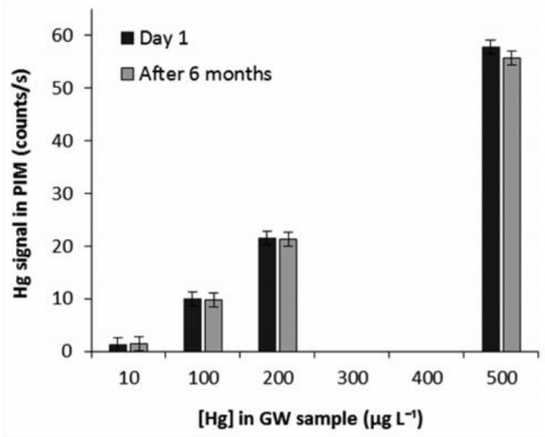


Use of membranes and disks



Parameter	Analytical feature
LOD	**0.2 µg L^{-1}** **(<1µg L^{-1})**
Linear range	0.6-10 µg L^{-1}
R^2	0.997
Method precision: n=8. 1 measurement (6 µg L^{-1})	RSD: 16.5%

G. Elias et al., **Analytical Chemistry 90 (2018)4756**

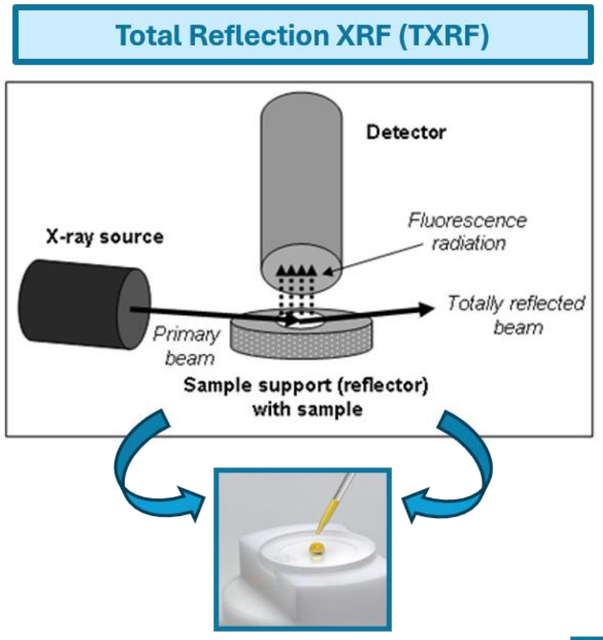


IL-PIM as a sorbent: a suitable storage medium?

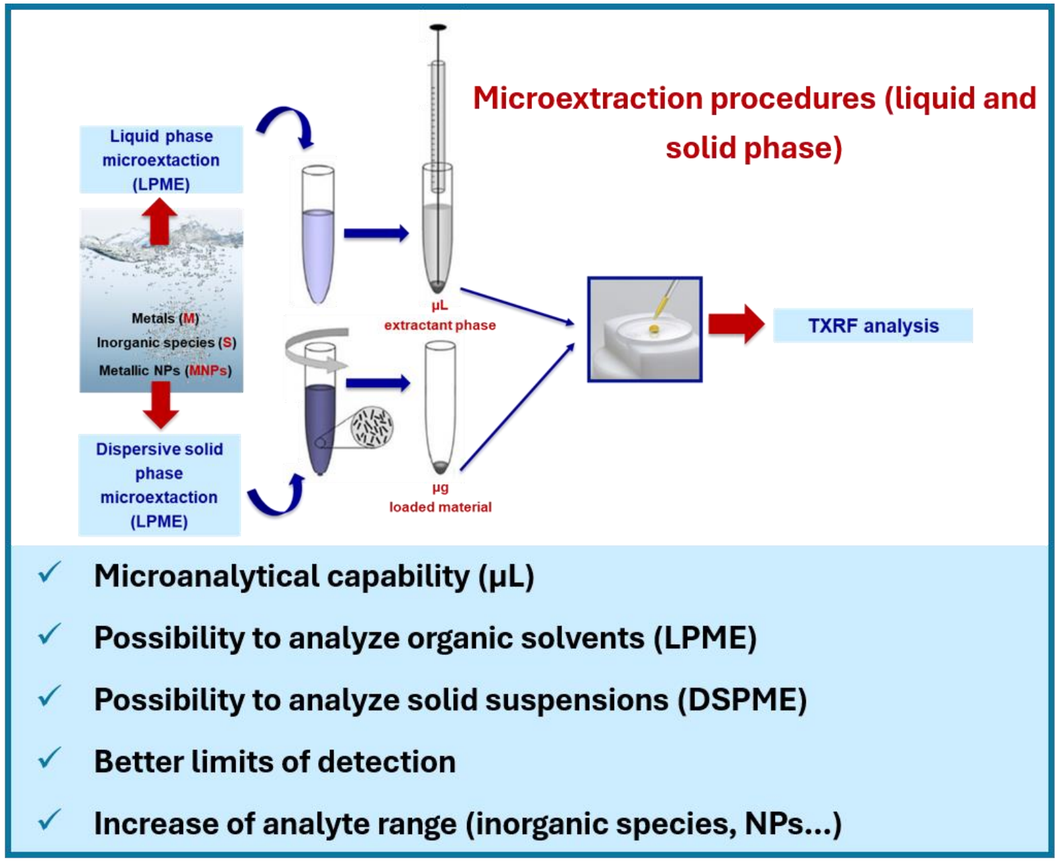
Critical stages and examples of XRF applications

Sample Preparation

Enhancing the analytical performance of TXRF for the analysis of liquid samples



Micro-sample prepared as a thin layer on a reflective carrier



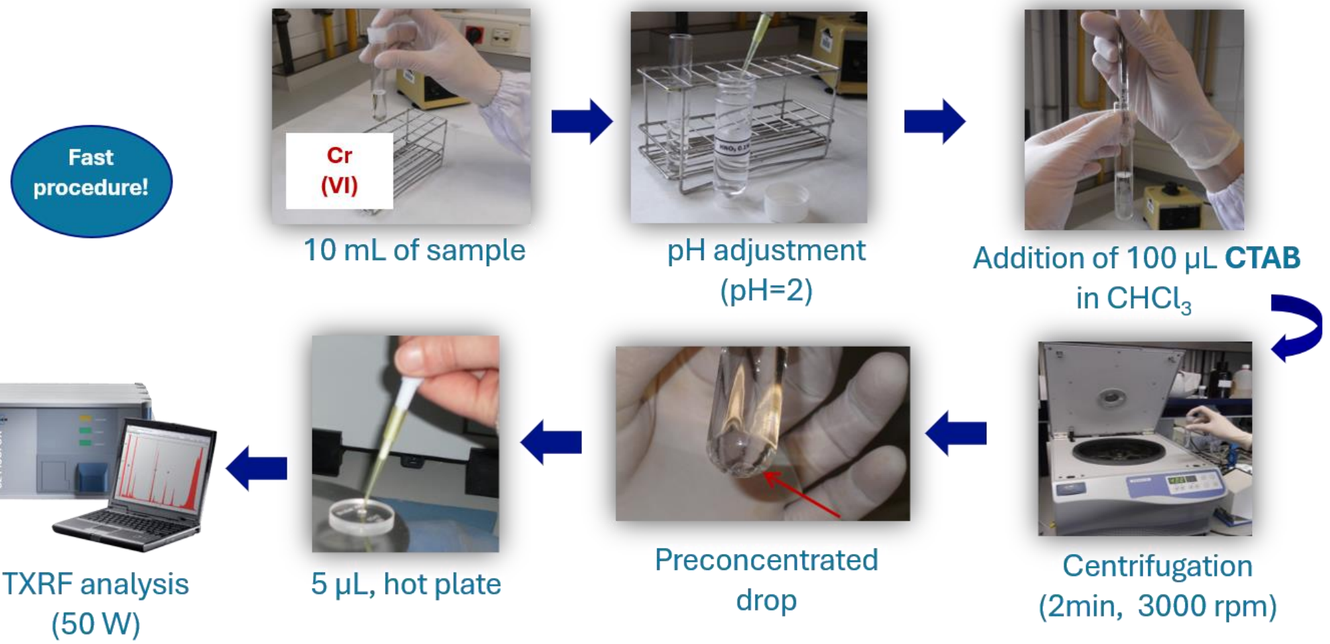
Concluding remarks and future perspectives

Sample Preparation

Enhancing the analytical performance of TXRF for the analysis of liquid samples

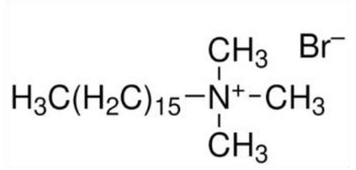
Liquid phase microextraction and TXRF analysis

Determination of Cr (VI) in concrete water extracts



UNE-EN 196-10:2008

- **Limit of detection: 0.9 µg/L**
- Linear range: 5-5000 µg/L
- Method precision (n=6): RSD=15.4% (25 µg/L), RSD=11.7% (200 µg/L)



CTAB
(Cetyltrimethylammonium bromide)

Analytical Application

Sample	DLLME TXRF method	Reference method
Clinker-1	2.5±0.3	2.28±0.4
Clinker-2	6.5±0.6	6.10±0.4

Marguí and Torrent. **Spectrochimica Acta Part B 204 (2023)106682**

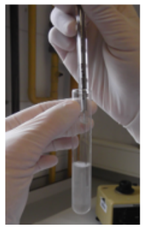
Critical stages and examples of XRF applications

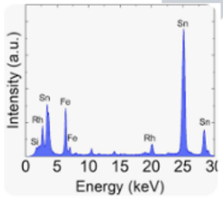
Sample preparation

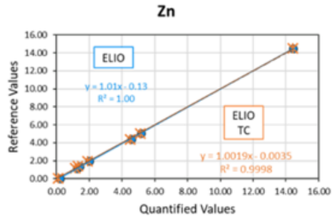
Hardware

Quantification

XRF results







Critical stages and examples of XRF applications

Hardware

X-ray tubes

- Reduction in size
- Decrease of the divergence beam
- Possibility of micro sources
- Liquid metal jet X-ray sources (Ga)

↓

- New portable XRF systems
- Improvement μ-XRF systems
- Improvement of the brightness

Detectors

- Design of silicon drift detectors (SDD)
- Air cooled detectors
- Windows based on graphenic carbon

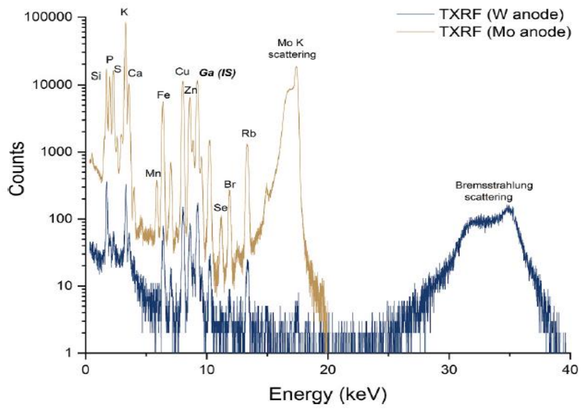
↓

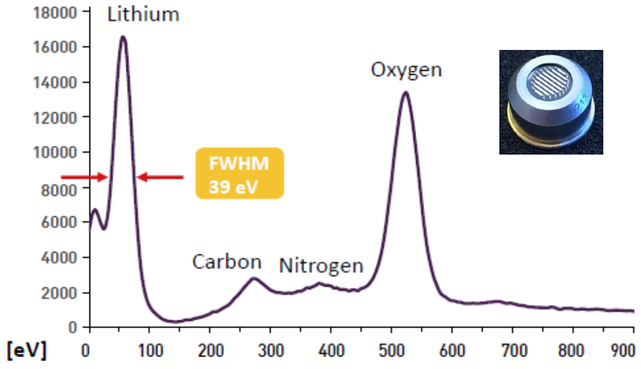
- Efficiency and resolution improvement
- New portable XRF systems
- Determination of light elements

Enhancing the analytical performance of XRF

↓

Novel interesting applications in the next future





KETEK GmbH, Munich, Germany, 2019

CA24131 - European Network for radiation-detection based Research and Innovation addressing increasing societal CHallenges (ENRICH)

Working Groups

Number	Title	Leader
1	Community Coordination	Dr Francesca BONFIGLI
2	Technological Advancement	Prof Leonardo ABBENE
3	Software Advancement	Dr Manuel SANCHEZ DEL RIO
4	Electronics and DAQ	Dr Chris ARMSTRONG
5	Multidisciplinary and Societal Applications	Dr Ivana TUCAKOVIĆ
6	Integration and Interchange	Dr Uddhab CHAULAGAIN
7	Mentoring, Training, and Dissemination	Dr Michela ESPOSITO

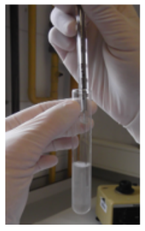
Critical stages and examples of XRF applications

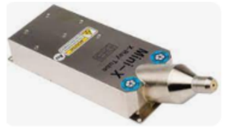
Sample preparation

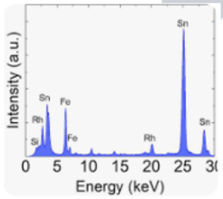
Hardware

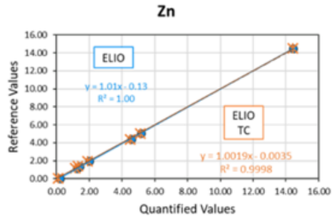
Quantification

XRF results



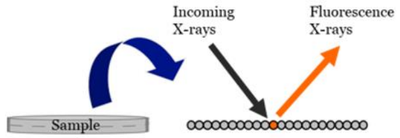






Critical stages and examples of XRF applications

Quantification



Quantitative XRF analysis

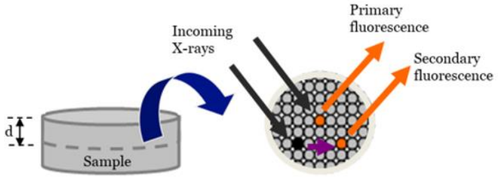
Type of sample

Thin samples

- Intensity is proportional to analyte concentration
- Matrix effects are negligible
- Examples: aerosol filters, liquids deposited on a carrier

Intermediate / thick samples

- Intensity is not proportional to analyte concentration
- Matrix effects correction methods are necessary
- Examples: pellets, fused beads, powders…



Quantification approaches

Matrix correction models required

Instrumental software

Internal Standardization

- Only TXRF
- No matrix-matched standards are needed
- Addition of an internal standard

Empirical calibration

- Set of standards similar to real samples
- Standards: CRMs, synthetic standards, secondary standards

Fundamental parameters

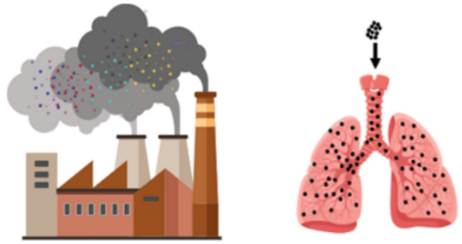
- Information about sample composition is needed
- Few pure elements or CRMs may be used as standards

Lack of suitable RM

Development of fit-for-purpose reference materials and guidance methods for employing them

Critical stages and examples of XRF applications

Quantification



Increasing concern about air particulate matter (APM) on human health

APM Sampling

PM collected on filtering membrane (Teflon)

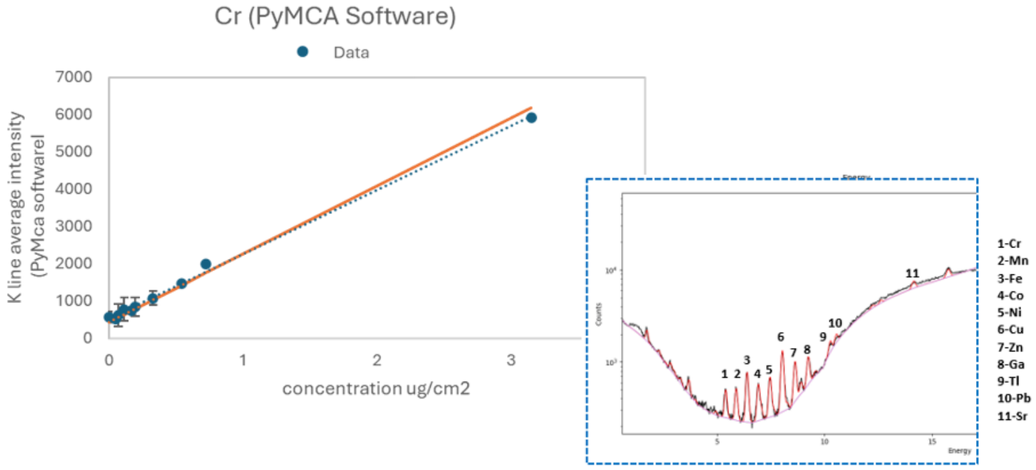
APM analysis

Reference methods: AAS, ICP
ISO Standard: EN 14902:2005

Acid digestion → ☒ Low recoveries

XRF/TXRF analysis

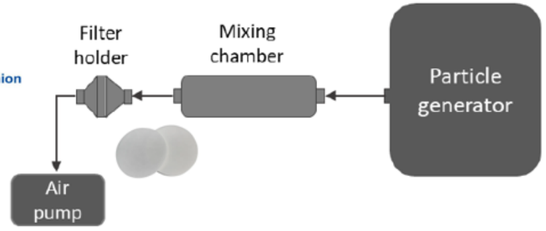
Direct analysis of the filter → ☒ **Lack of RM**



Preparation of reference materials

AIRCAL

cost EUROPEAN COOPERATION IN SCIENCE & TECHNOLOGY — Funded by the European Union



- RM are prepared by nebulization
- By varying nebulization time different mass loadings are obtained
- Generation of particulates with tunable composition range

Critical stages and examples of XRF applications

Quantification

Quantitative XRF analysis

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Matrix correction models required

Fundamental parameters

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- Few pure elements or CRMs may be used as standards

Use of the whole XRF spectrum for quantification: CHEMOMETRIC TOOLS

Critical stages and examples of XRF applications

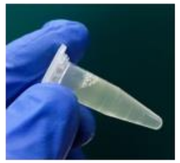
Quantification

CHEMOMETRICS + XRF

→ QUANTITATIVE ANALYISIS

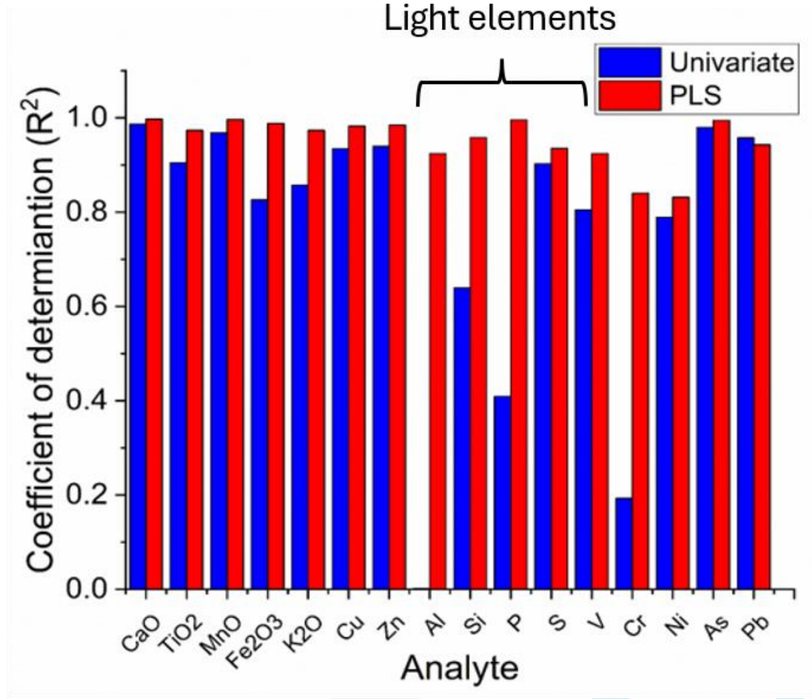
- Improvement of sensitivity and accuracy
- Extend the application of XRF systems:
  - Determination of light elements

Analysis of marine sediments



- 20 mg powder sediment
- 1 mL 1% (v/v) Triton X-100
- Vortex mixing, 1 min
- 5 µL sample deposition volume

- **TXRF analysis** (benchtop system)



Coefficient of determination obtained for a set of marine sediment reference materials using univariate and PLS (using full raw spectroscopic data (whole spectrum)

PLS: Partial Least Squares analysis

Marguí et al., **unpublished data**

Future Perspectives

Sample preparation

- New simple sample treatment strategies aligned with **GAC** principles.
- Enhance the quality of in situ analyses

Hardware

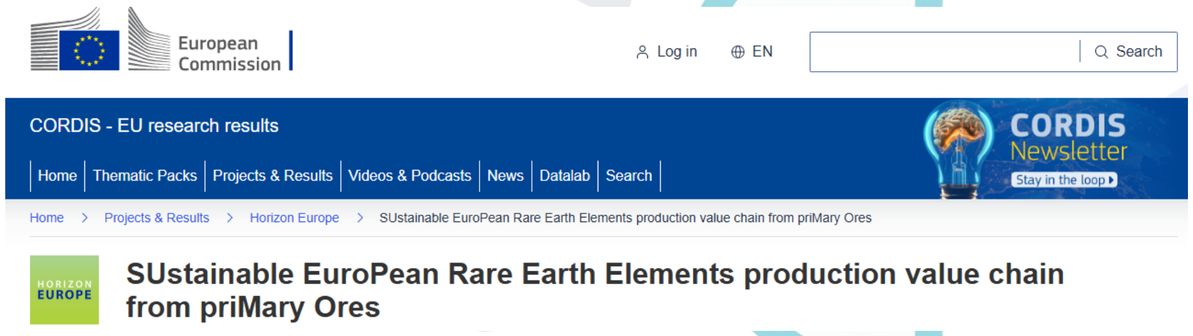
- Improved excitation / detection (increase sensitivity)
- Improved resolution
- Software?

Quantification

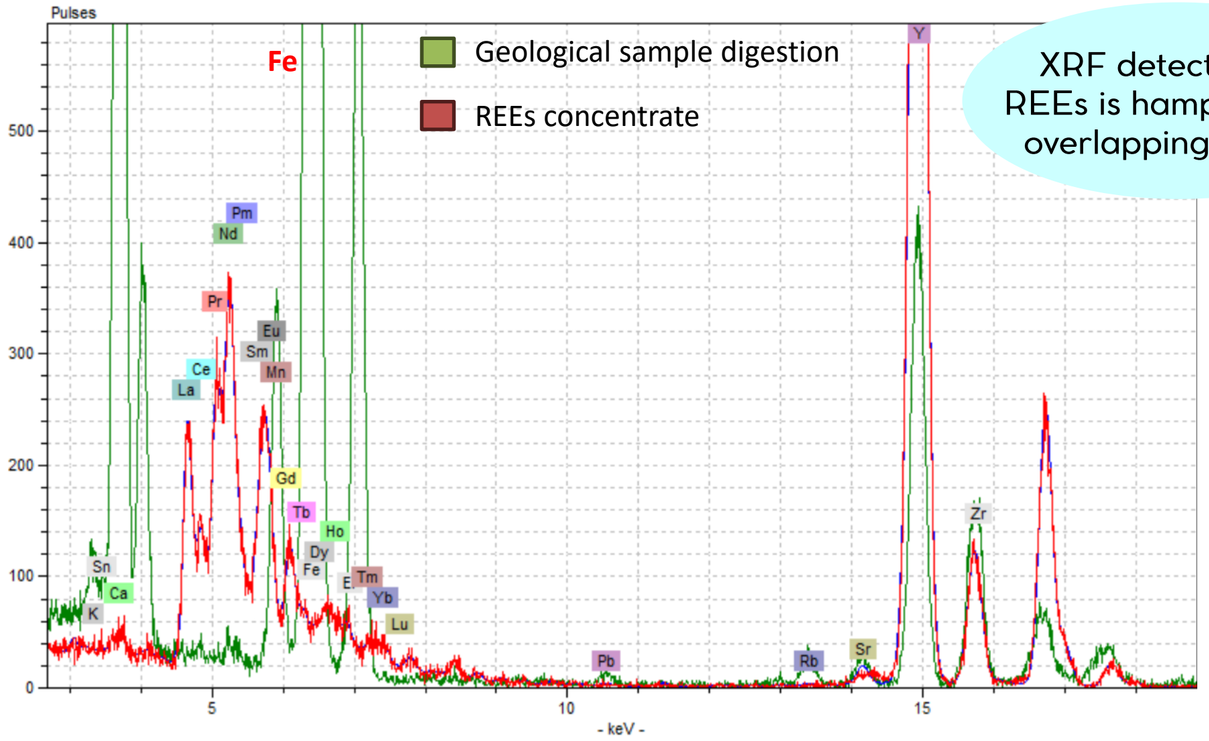
- Development of adequate Reference materials (solid samples)
- Chemometric tools
- IA ??

XRF results

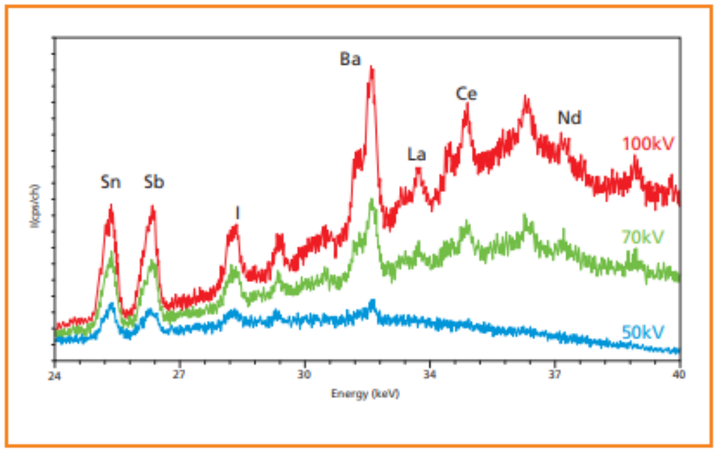
Determination of REEs (Rear Earth Elements) in geological materials and liquid solutions by XRF…



Determination of REEs (Rear Earth Elements) in geological materials and liquid solutions by XRF…



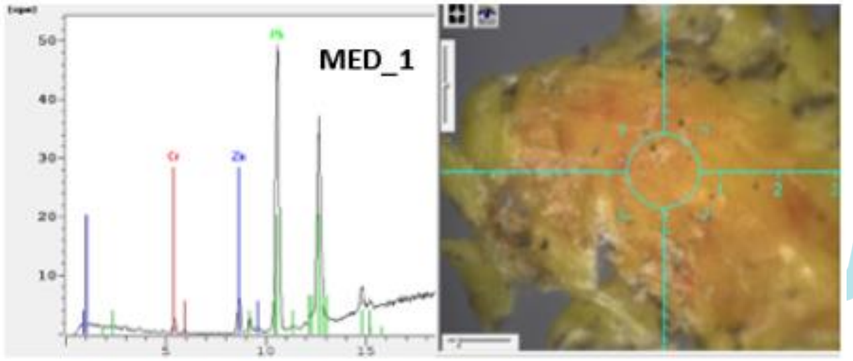
TXRF spectra (S2 PICOFOX, W X-ray tube)

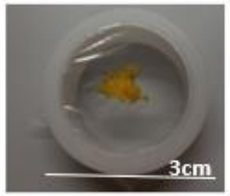


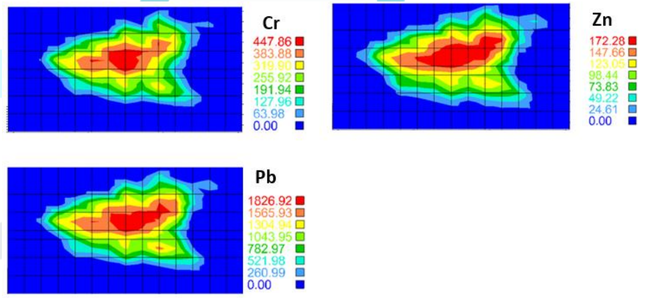
High-voltage Gd or Sc/W X-ray tube (1)
Operating at a maximum power of 600 W and voltages between 25 kV and 100 kV, PANalytical's patented X-ray tubes are unique among EDXRF spectrometers. The characteristic tube lines of the Gd-anode enhance the fluorescence of elements in the range of rhodium to barium, while the Sc tube lines of the Sc/W tube enhance the fluorescence of lighter elements. The tube's 100 kV capability has advantages for the excitation of heavy element K-lines.

Epsilon 5 (Panalytical) – Some years ago…

Quantification of metals in Microplastic samples (<5,0mm) by μ-XRF







Measurement conditions:

- *15x15 (225 measurements)*
- *Col 1 mm*
- *50kV, 100 μA, 50 s*

- Lack of suitable Standards
- Thickness correction needed

Concluding Remarks

The ENRICH COST Action provides a unique opportunity to bring together analytical chemists, physicists, instrument developers, engineers, software specialists, and end-users to accelerate innovation and expand the applicability of XRF technologies.

Acknowledgements

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COST (European Cooperation in Science and Technology) is a funding agency for research and innovation networks. Our Actions help connect research initiatives across Europe and enable scientists to grow their ideas by sharing them with their peers. This boosts their research, career and innovation.

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