Materials design & selection for Circular Economy

Module 3: Molecules and materials chemico-physical characterisation

Academic year 2026/2027

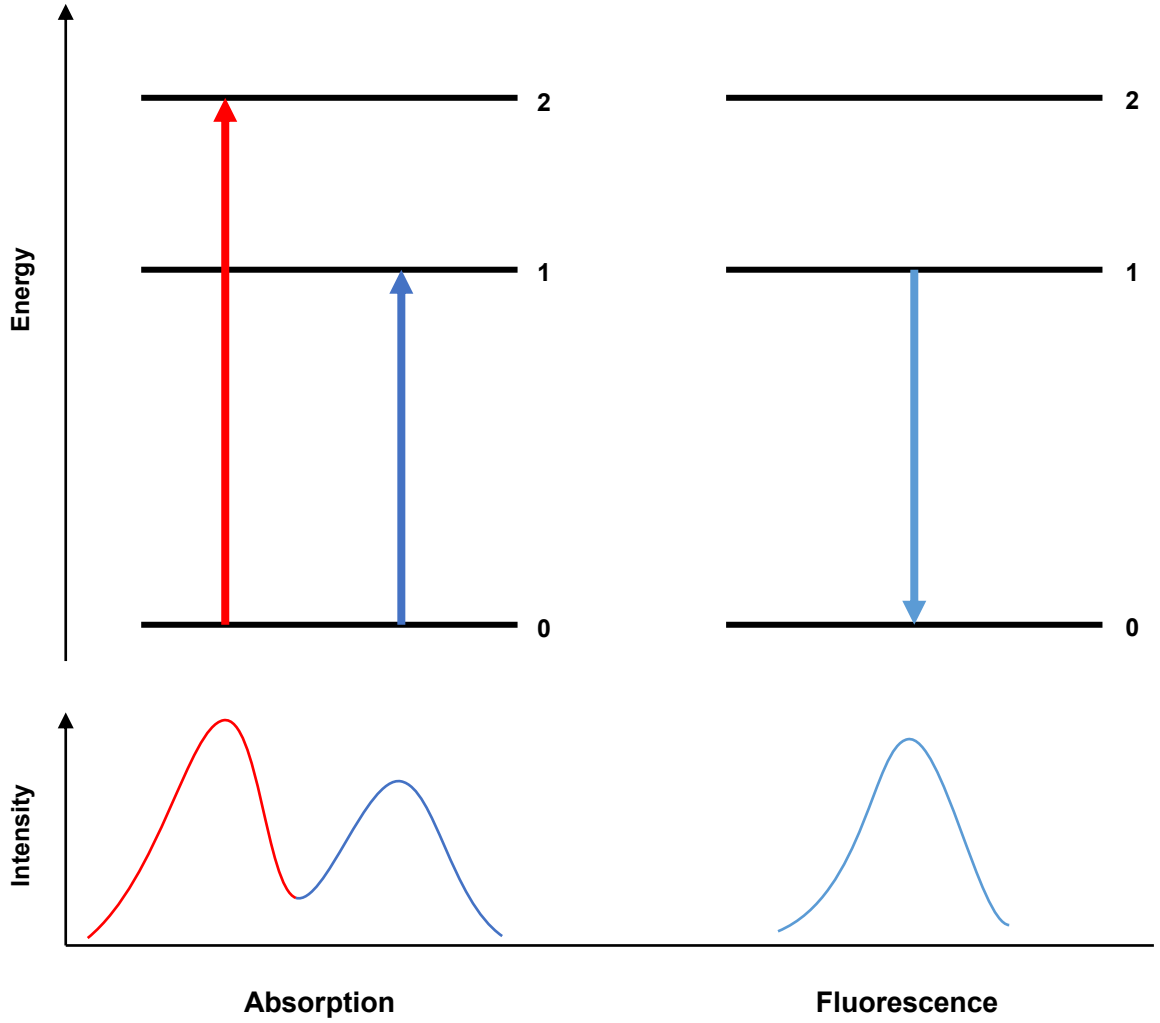
Lecturer: **Paolo Dolcet**

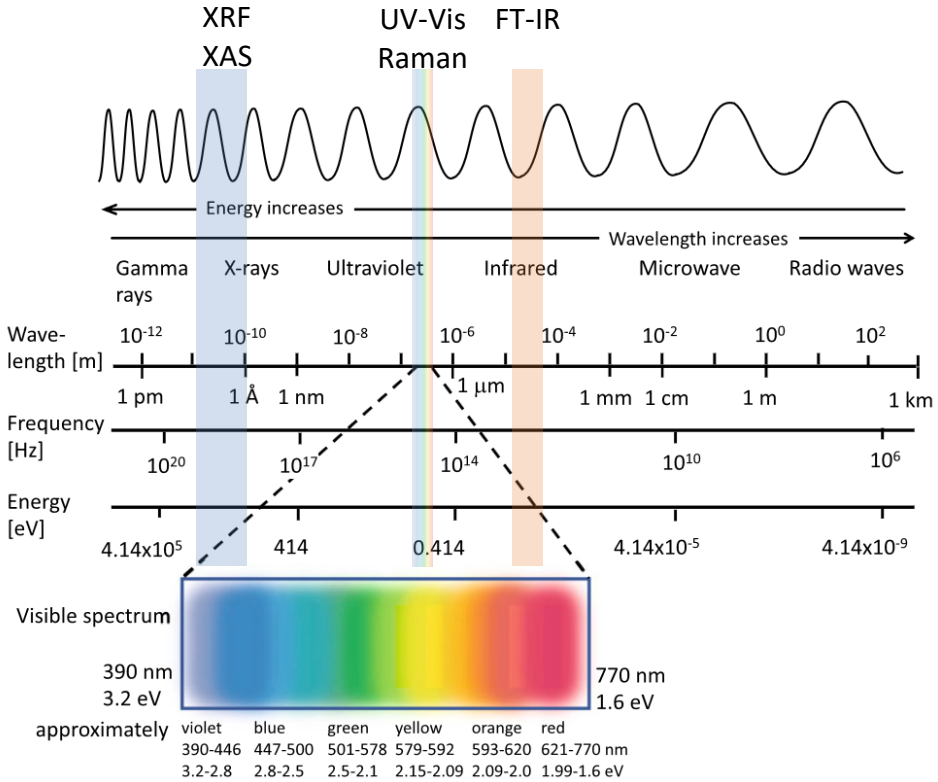
Spectroscopies across the CRM value chain

- Exploration and Field-Scale detection
  - XRF
  - LIBS
- Ore characterization and mineral mapping
  - XRF
  - ICP-OES/MS
  - FT-IR/Raman
  - XPS
- Process monitoring and recycling
  - FT-IR/Raman
  - ICP-OES/MS
  - UV-Vis
- Waste valorization and multi-scale integration
  - XRF

Typical samples:
Complex, multi-element matrices
Trace levels

Basics of spectroscopy

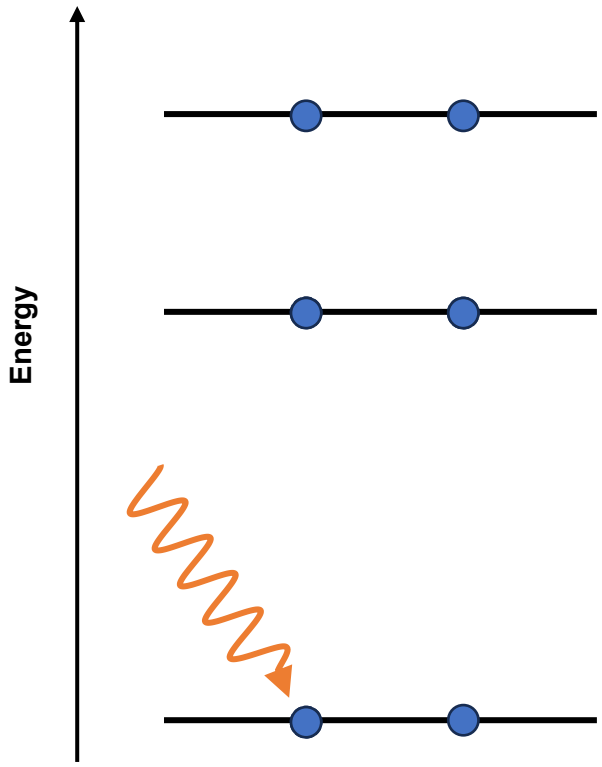




UV-Vis, ICP-OES, XRF, XPS: electronic levels
FTIR and Raman: vibrational levels

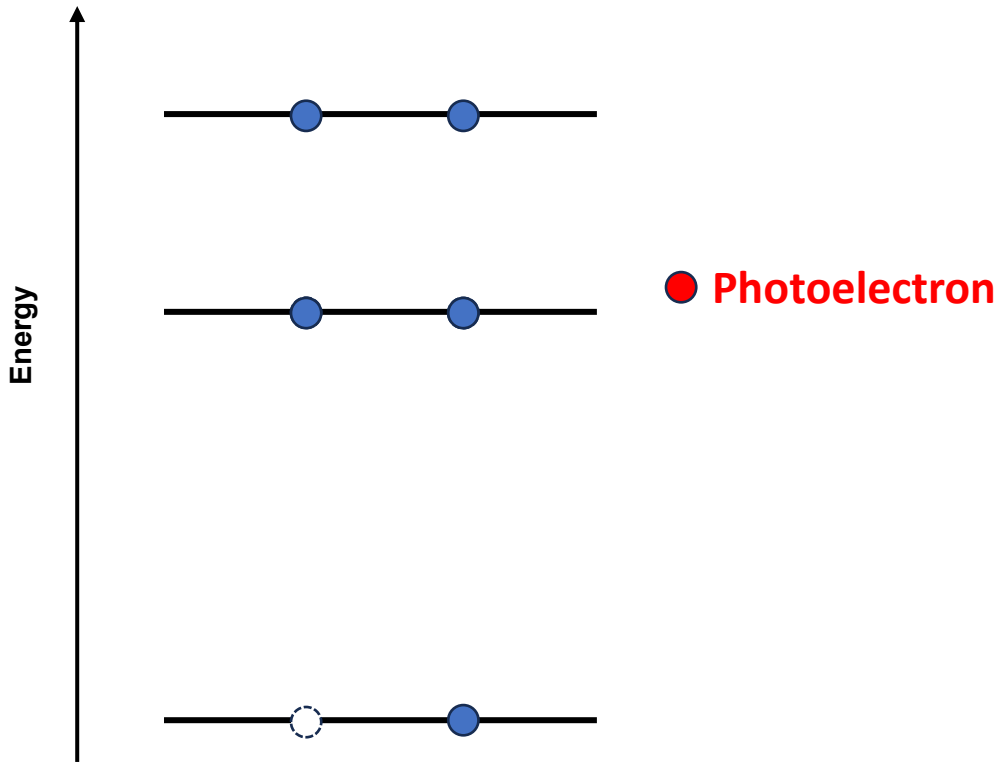
Each transition is a «fingerprint» of a specific species

X-ray fluorescence



- X-ray fluorescence: emission of secondary X-rays after irradiation with X-rays (or γ rays)
- X-ray fluorescence is characteristic for each element → characteristic X-rays (or line)

X-ray fluorescence



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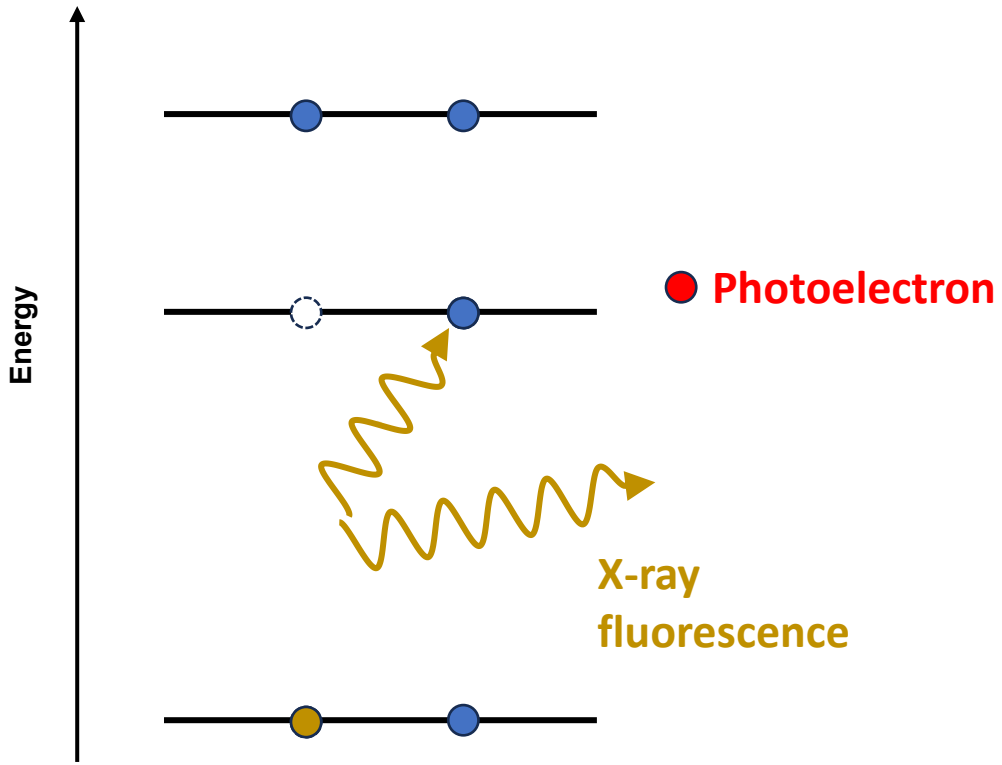

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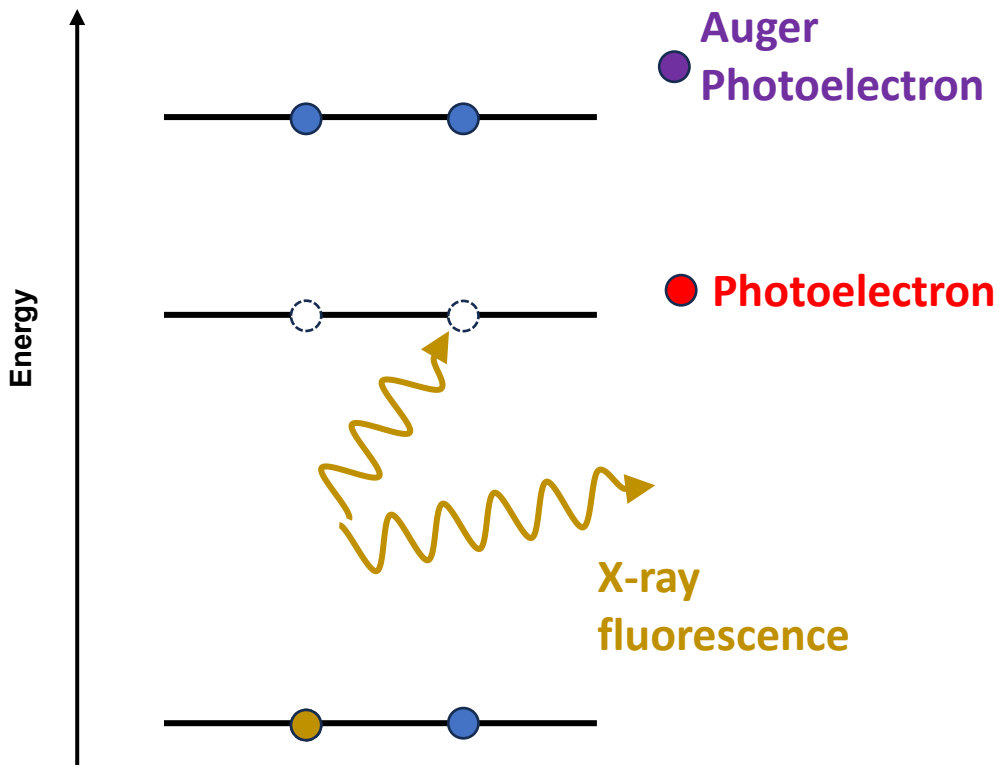

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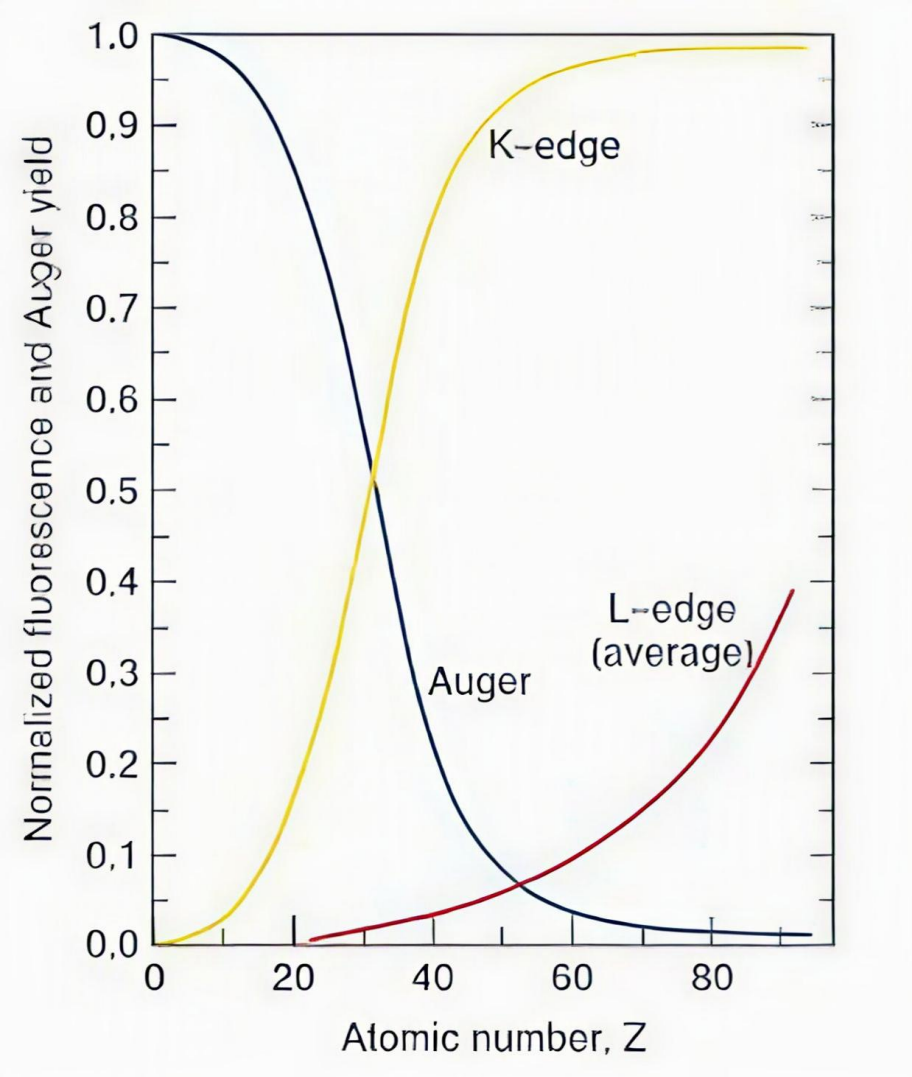


- X-ray fluorescence: emission of secondary X-rays after irradiation with X-rays (or γ rays)
- X-ray fluorescence is characteristic for each element → characteristic X-rays (or line)
- **Fluorescence yield** ω_i

$$\omega_i = \frac{Z^4}{A_i + Z^4}$$

Constant depending on the type of line

- **Moseley's law**

$$\nu = A \cdot (Z - b)^2$$

Frequency of characteristic X-ray

Constants depending on the type of line

X-ray fluorescence nomenclature

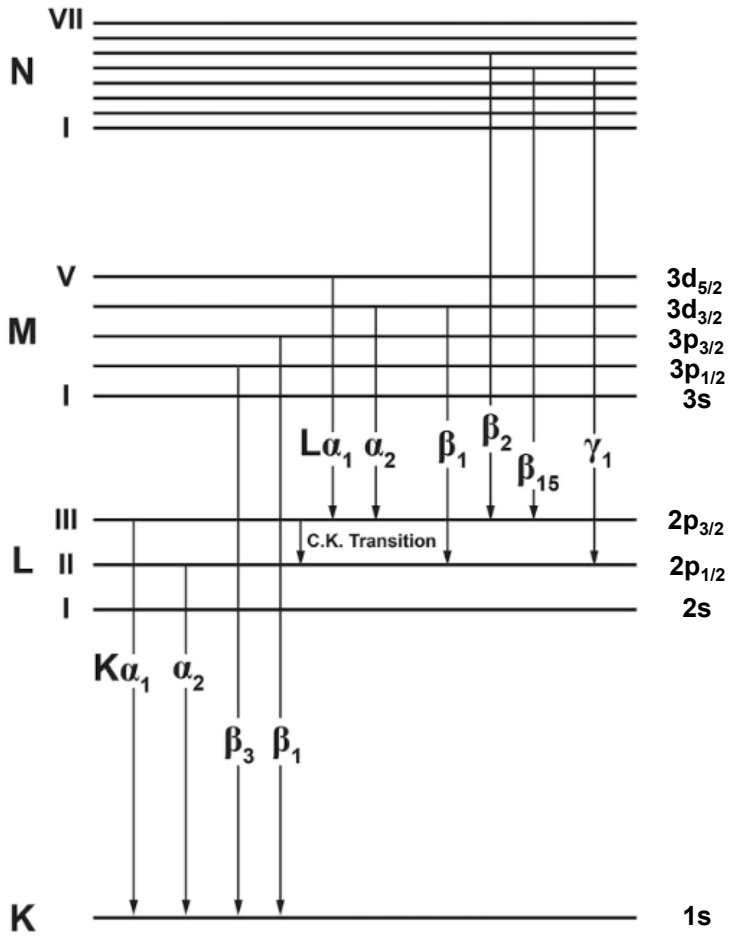
Siegbahn notation (1916)

$K\alpha_1$: transition from the most energetic L level to the K level

$K\alpha_2$: transition from the 2nd most energetic L level to the K level

$K\beta_1$: transition from the most energetic allowed M level ($\Delta l = \pm 1$) to the K level

α transitions are more intense than β



IUPAC notation

$K\text{-}L_3$: transition from the most energetic L level to the K level

$K\text{-}L_2$: transition from the 2nd most energetic L level to the K level

$K\text{-}M_3$: transition from the most energetic allowed M level ($\Delta l = \pm 1$) to the K level

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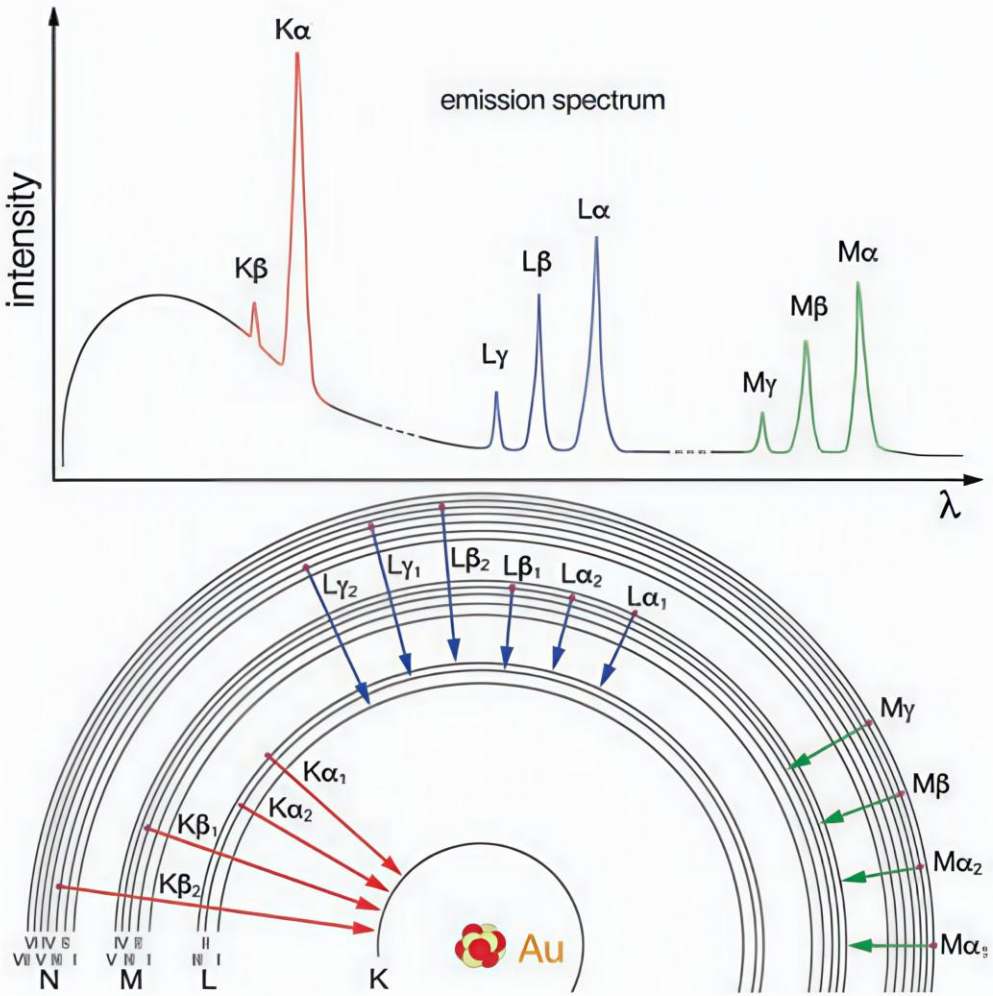

AC notation

: transition from the most energetic
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: transition from the 2nd most
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3: transition from the most
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X-ray fluorescence spectroscopy

Radiation: X-rays (5-60 keV)

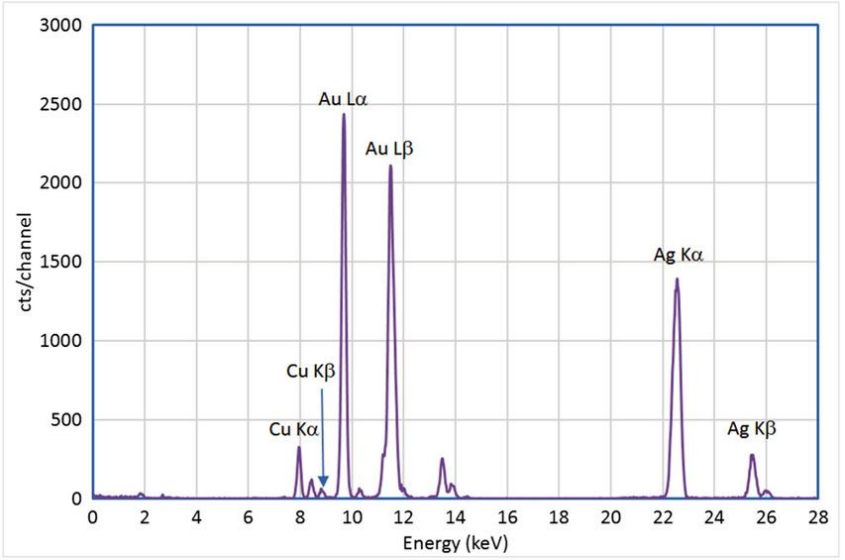
Quantitative elemental composition

Atomic number ↓ Fluorescence yield ↓

Pros:
- Rapid and non-destructive* analysis
- Minimal to no sample preparation (surface cleaning)
- Portable

Cons:
- Cannot determine elements Z < 10
- Requires licensing, safety training and operating precautions





Nat. Rev. Meth. Prim., 2025, 5:17
Rad. Phys. Chem., 2020, 170, 108666
Chemosensors 2025, *13*(2), 41

X-ray fluorescence spectroscopy

Two types of XRF:

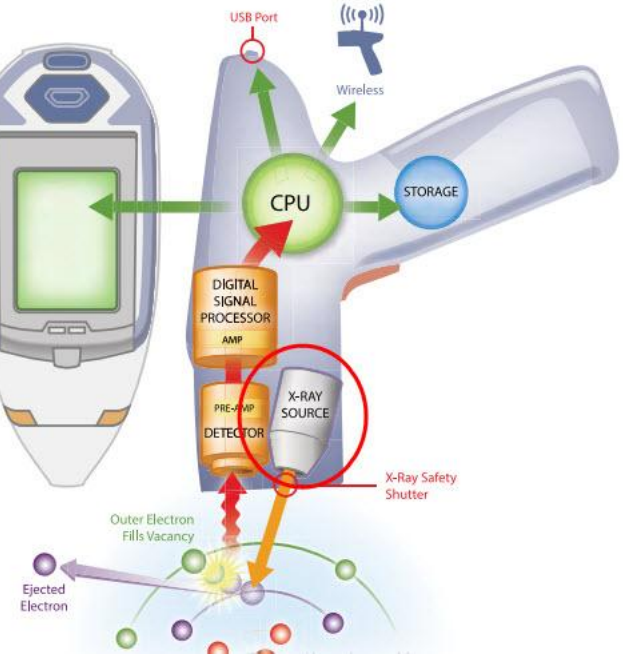
- **Energy dispersive**: measures all emitted energies simultaneously (faster, higher LOD)
- **Wavelength dispersive**: analyses wavelength selectively (higher resolution, lower LOD)

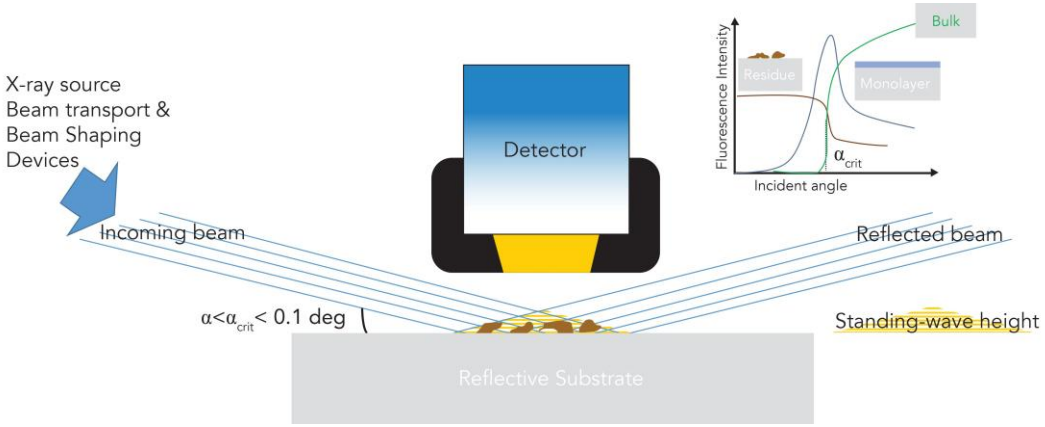
Portable devices are energy dispersive XRF

LOD of portable devices ca. 10 higher

Total reflection XRF (TXRF) improves the LOD (requires polished surface)

Total reflection strongly limits background noise





https://www.spectroscopyonline.com/view/the-fundamentals-of-total-reflection-x-ray-fluorescence

SEM-EDS

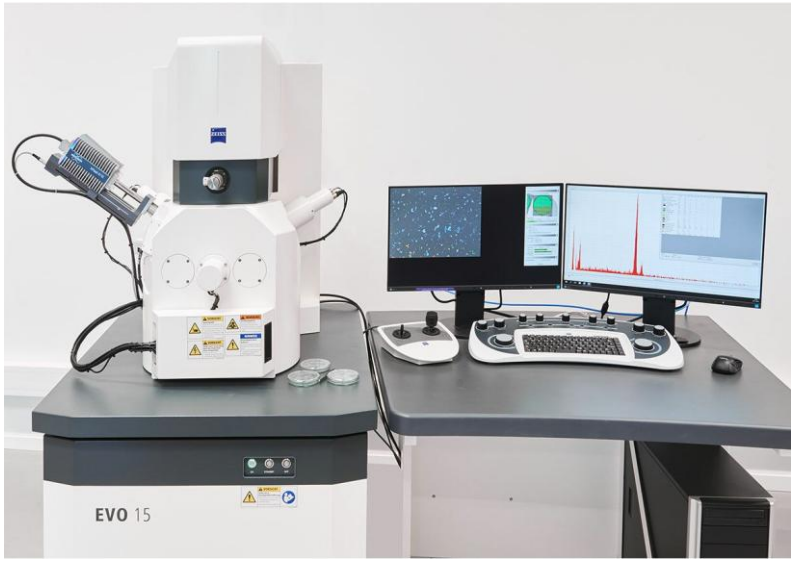
Provides chemical information together with morphological information

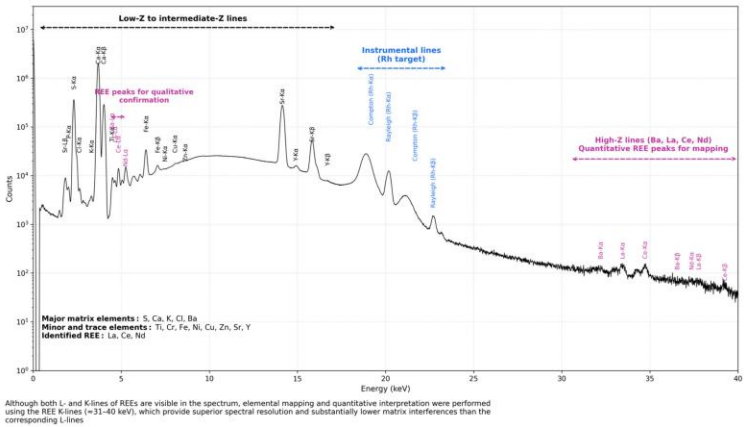
Basic principles similar to XRF

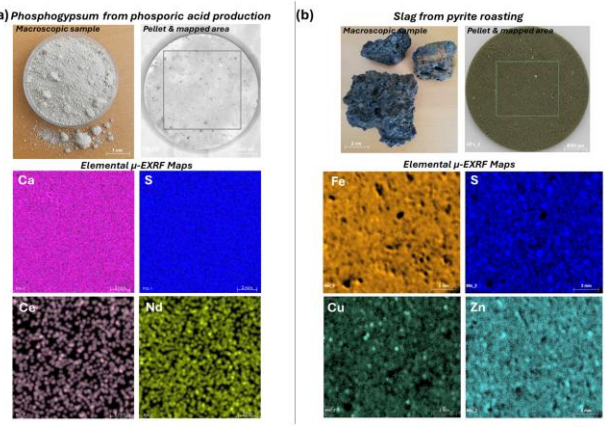
More surface sensitive than XRF

Pros:
- High spatial resolution
- Chemical information

Cons:
- Slow method
- Requires dedicated EM equipment
- Might require complex sample preparation







Minerals **2026**, *16*(8), 803

ICP-OES/ICP-MS

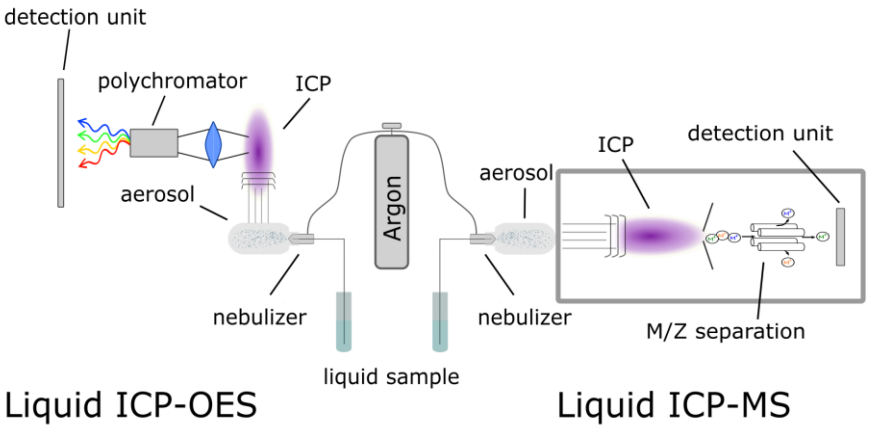
Family of techniques in which the sample is atomized/ionized by a plasma

Signal:
- Optical emission spectroscopy (OES): Light emitted by excited atoms
- Mass Spectrometry (MS): Mass-to-charge ratio of ions

OES preferred for bulk verification, MS for low-concentration of high-value elements (REEs or PGMs)

Pros:
- Very low detection limits (ppb-ppm for OES, ppq-ppt for MS)
- High accuracy
- MS can distinguish isotopes

Cons:
- Requires complex sample preparation (digestion)
- High costs (instrument and operation/maintenance)
- Complex matrices lead to severe overlaps in ICP-OES



https://www.tuwien.at/en/tch/lalibs/techniques/icp-ms-icp-oes
https://www.spectro.com/inductively-coupled-plasma-mass-spectrometry-icp-ms-principle
Talanta, 2026, 303, 129478

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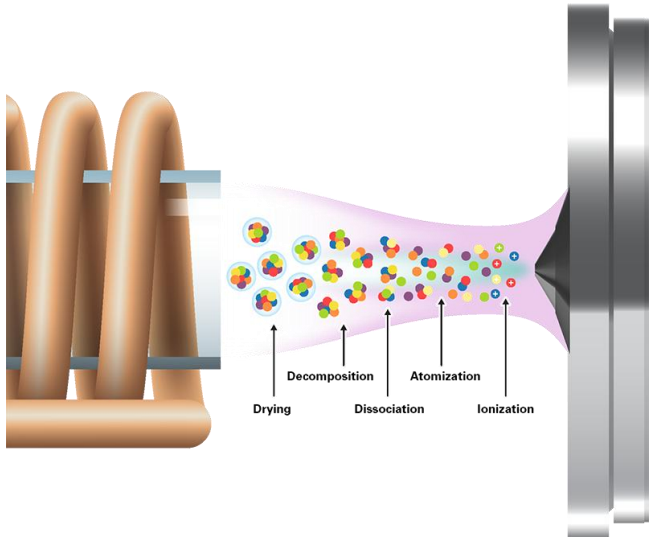

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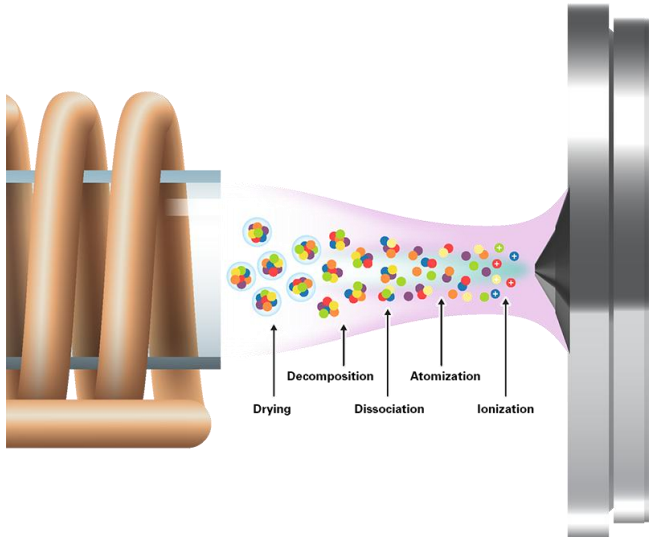

Table S1 Chemical analysis of relevant matrix composition in Mn ores by XRF

Mn ore	Zamb. lump	Nch. lump	SARM 16	SARM 17
Mn	42.03	45.35	49.7	38.81
MnO2	62.78	37.62	31.6	28.2
Fe	0.7	9.88	11.48	4.27
Al2O3	1.31	0.35	0.3	0.24
CaO	0.3	7.24	4.7	14.4
MgO	<0.03	1.15	0.76	3.03
SiO2	9.51	3.78	5.04	4.69
Mn/Fe	60.04	4.59	4.32	9.08
P	0.206	0.036	0.033	0.018
S	<0.01	0.061	0.17	0.01
BaO	10.02	0.3	0.6	0.08

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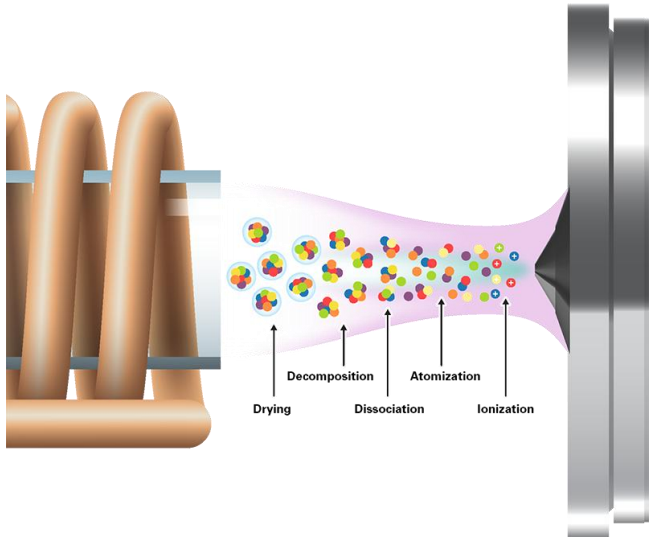

Table 3
ICP-MS results of Mn ores samples, using glass beads. Concentrations (C) are expressed in ppm (mg kg-1) with relative standard deviation expressed in %.

REE	Nchwaning lump		Zambian lump		SARM 16		SARM 17	
	C (mg kg^{-1})	RSD %	C (mg kg^{-1})	RSD %	C (mg kg^{-1})	RSD %	C (mg kg^{-1})	RSD %
Y	13.74	2.13	50.31	0.68	12.00	1.13	7.59	4.54
La	6.55	0.91	32.73	1.25	6.92	4.22	4.39	1.63
Ce	8.64	0.33	98.56	0.58	8.73	2.16	4.84	1.75
Pr	1.13	2.12	12.42	0.91	1.15	0.90	0.76	3.22
Nd	4.98	1.20	53.65	1.81	4.92	5.86	3.22	5.68
Sm	1.13	4.28	15.47	2.60	1.09	12.89	0.63	7.83
Eu	0.40	14.10	6.35	2.07	0.47	6.27	0.16	5.14
Gd	1.36	4.81	13.68	2.95	1.25	5.34	0.86	3.88
Tb	0.22	3.19	2.06	2.11	0.19	9.73	0.13	2.70
Dy	1.48	2.93	11.85	1.58	1.29	1.28	0.84	6.62
Ho	0.37	4.03	2.24	0.86	0.32	3.23	0.21	5.82
Er	1.16	2.24	5.84	4.37	0.91	3.60	0.62	3.88
Tm	0.26	8.27	0.90	2.18	0.23	6.33	0.20	5.62
Yb	1.14	7.59	6.01	1.68	0.92	5.60	0.66	10.57
Lu	0.20	7.22	0.75	0.74	0.17	5.66	0.11	12.78

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Laser Ablation-ICP-MS

Emerging technique: Laser Ablation-ICP-MS (LA-ICP-MS)

LA-ICP-MS offers direct solid sampling & mapping

Laser performs microdestructive sampling of the sample

It requires laser parameter optimization

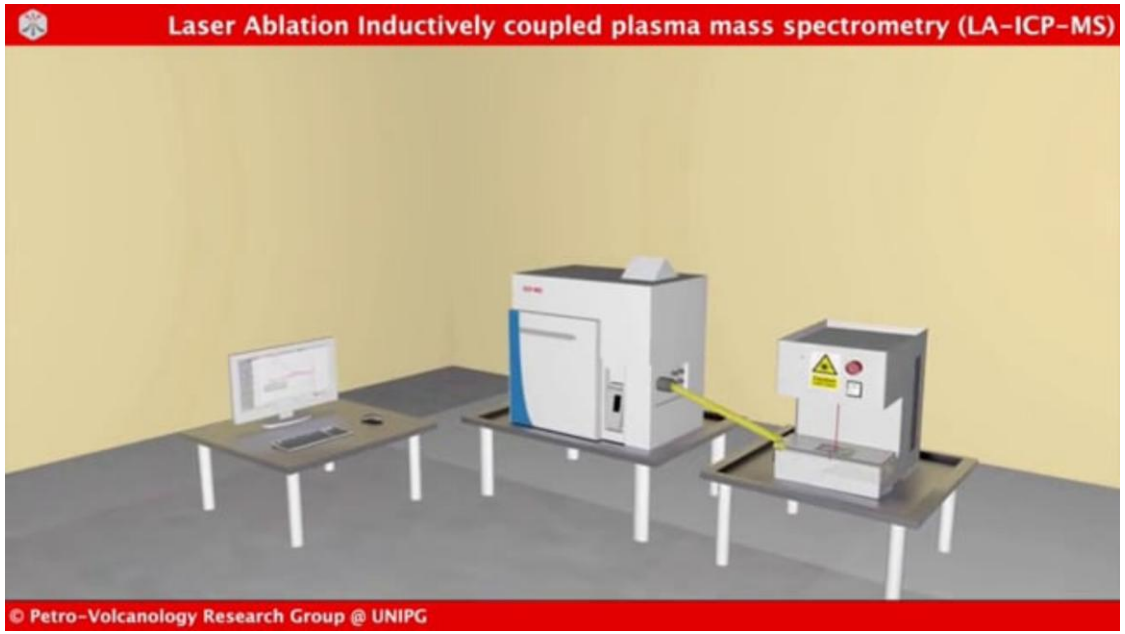
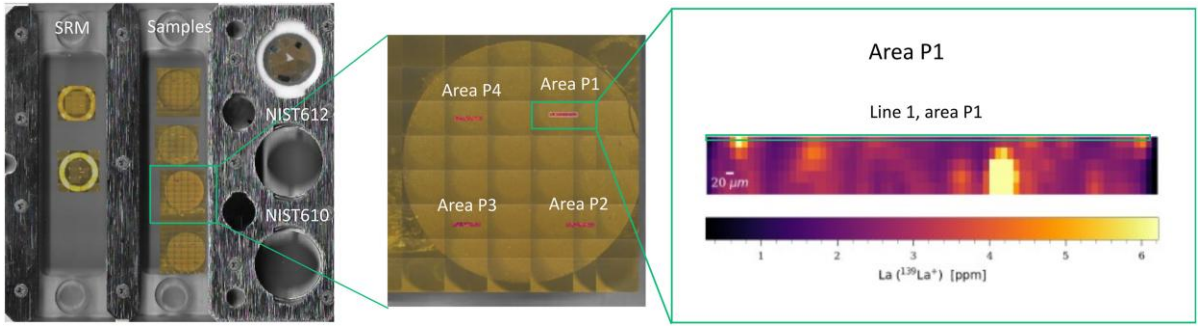


Table 7
LA-ICP-MS results of Mn ores samples, using pressed pellets. Concentrations (C) are expressed in ppm (mg kg-1) with relative standard deviation expressed in %.

REE	Nchwaning lump		Zambian lump		SARM 16		SARM 17	
	C (mg kg^{-1})	RSD %	C (mg kg^{-1})	RSD %	C (mg kg^{-1})	RSD %	C (mg kg^{-1})	RSD %
Y	12.39	5.54	67.11	3.64	10.04	9.05	6.56	7.29
La	7.78	4.07	39.20	3.32	6.12	10.37	4.64	8.98
Ce	9.24	12.52	121.40	4.88	15.37	35.63	4.36	5.91
Pr	1.12	4.91	11.49	3.96	0.87	7.73	0.66	8.91
Nd	6.13	18.73	63.04	2.62	4.21	8.48	2.98	1.89
Sm	1.35	10.43	16.57	4.50	0.86	5.40	0.58	5.58
Eu	1.74	6.98	16.93	7.33	1.39	9.75	0.27	4.00
Gd	1.42	2.75	15.66	3.91	0.99	13.43	0.66	10.91
Tb	0.21	4.28	2.25	4.51	0.13	12.24	0.11	1.00
Dy	1.32	7.17	12.84	4.55	0.89	14.12	0.64	6.98
Ho	0.31	4.85	2.31	4.87	0.21	11.23	0.15	6.19
Er	0.88	4.44	6.23	4.51	0.66	6.64	0.50	9.94
Tm	0.12	10.00	0.86	5.86	0.09	15.25	0.07	20.00
Yb	0.83	3.21	5.27	5.33	0.61	7.93	0.45	14.50
Lu	0.13	6.79	0.72	5.42	0.09	6.06	0.06	11.76



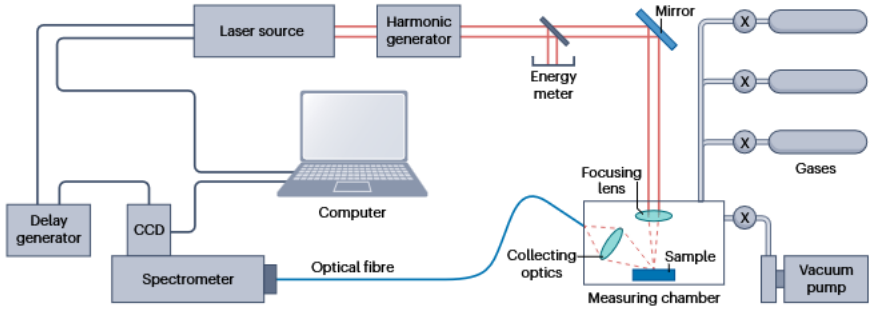
http://pvrg.unipg.it/laser-ablation-icp-ms/
Talanta, 2026, 303, 129478

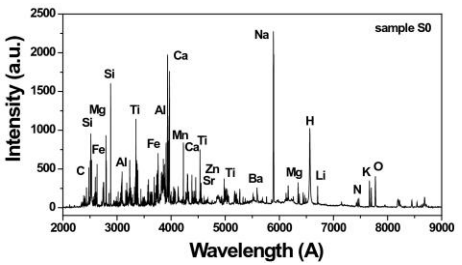
Laser-induced breakdown spectroscopy

"Emerging" atomic emission spectroscopic method

Used by NASA on the surface of Mars

Pulsed laser (typically Nd:YAG) is used to locally produce plasma of the sample





Pros:

- Rapid and non-destructive* analysis
- Minimal to no sample preparation
- Portable
- Works for light elements (Li, Be)

Cons:

- Relatively low accuracy (5-20 %)
- High limit of detection (ppm-%), element dependent

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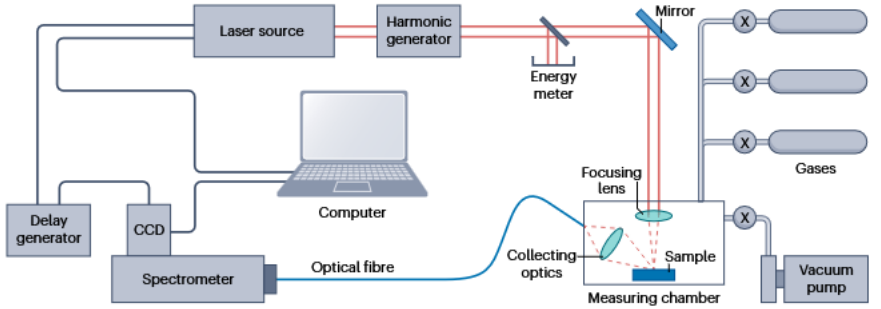

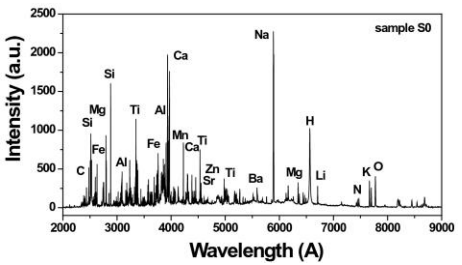

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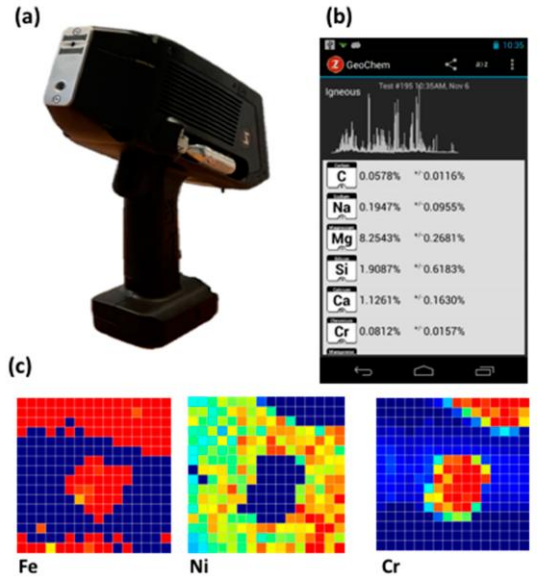

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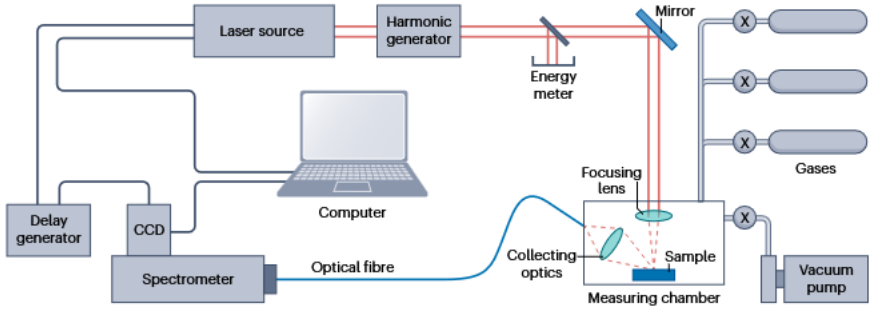
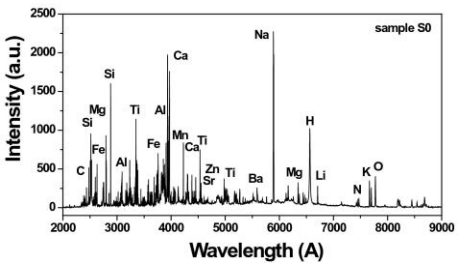
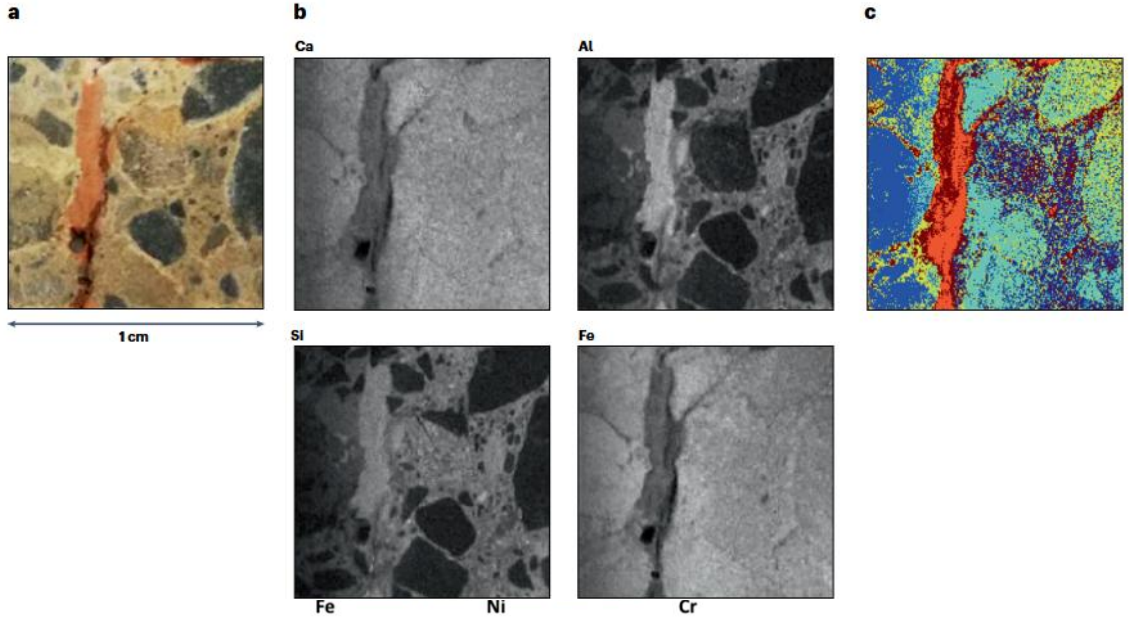






Nat. Rev. Meth. Prim., 2025, 5:17
Rad. Phys. Chem., 2020, 170, 108666
Chemosensors 2025, *13*(2), 41

Laser-induced breakdown spectroscopy

LIBS is a “real time” analysis (< 1s)

Full elemental composition with a single laser pulse

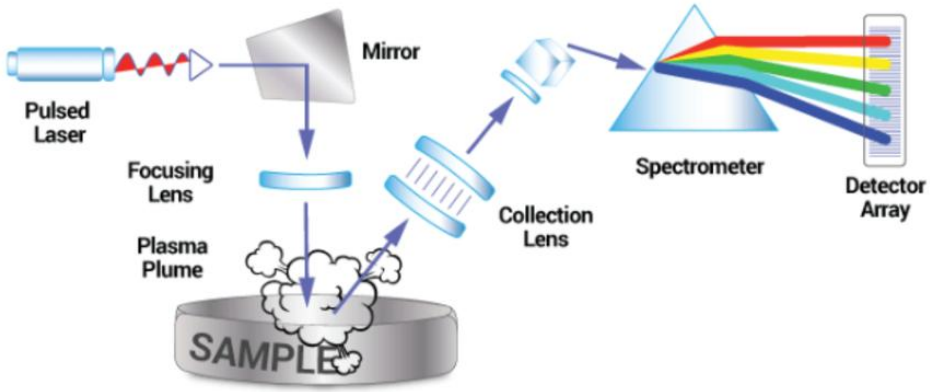
Small analytical spot size

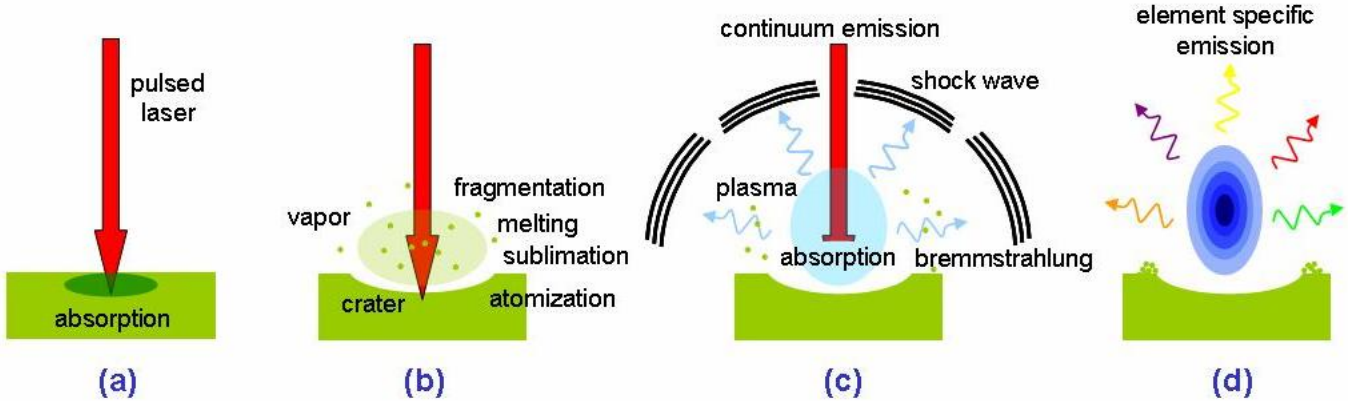
Only ng of samples needed

Microscale mapping possible

Quantitative analysis*

Destructive on the micrometer scale





Schematic of the laser-induced breakdown process.

https://libs-info.com/
https://www.worldoftest.com/it/articles/libs-analyzers-explained/
https://www.uwindsor.ca/people/rehse/299/libs
Spectrochim. Acta B, 2021, 175, 106013

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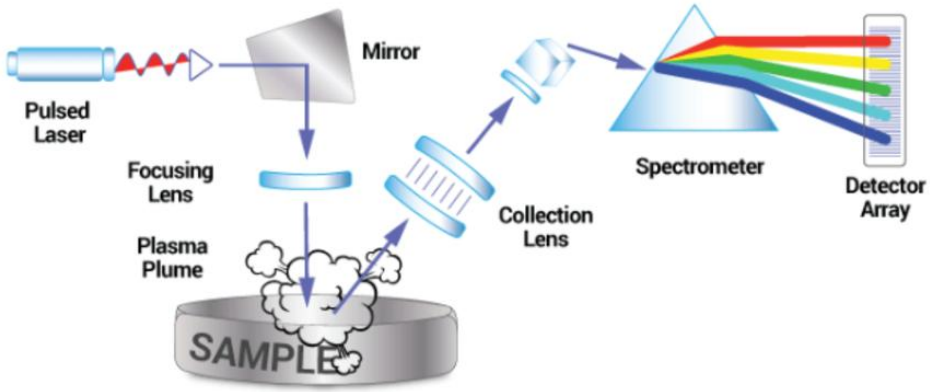
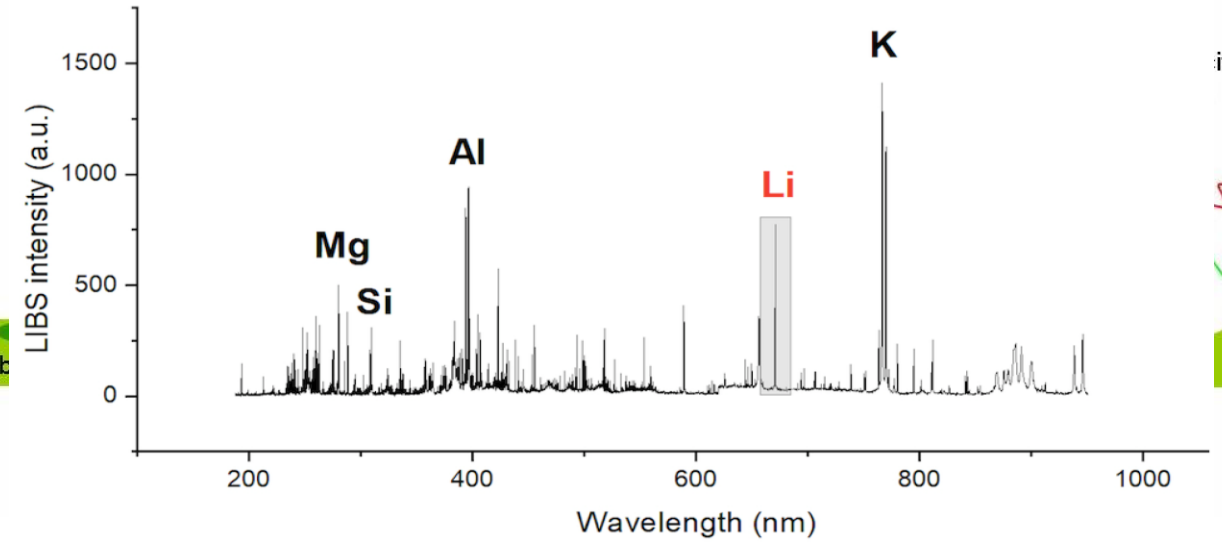




https://libs-info.com/
https://www.worldoftest.com/it/articles/libs-analyzers-explained/
https://www.uwindsor.ca/people/rehse/299/libs
Spectrochim. Acta B, 2021, 175, 106013

X-ray photoelectron spectroscopy

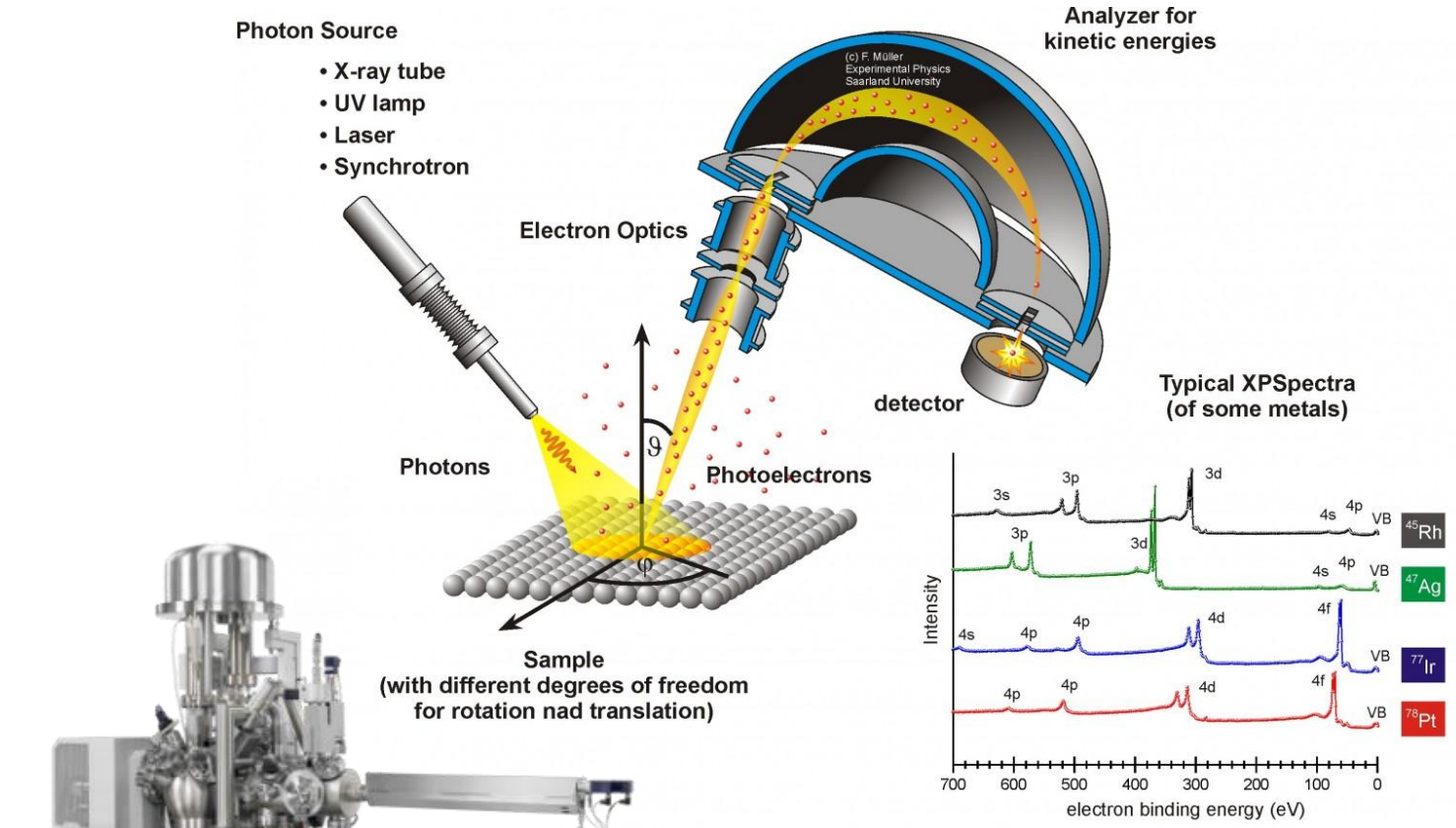
Surface sensitive method (ca. 10 nm max)

Multi-element chemical information

Can provide oxidation state of the elements

Pros:
- Atomic sensitivity
- Surface sensitivity

Cons:
- Requires UHV
- Slow method
- Expensive equipment



https://www.azom.com/equipment-details.aspx?EquipID=8848
https://www.findlight.net/blog/electron-spectroscopy-for-surface-analysis/

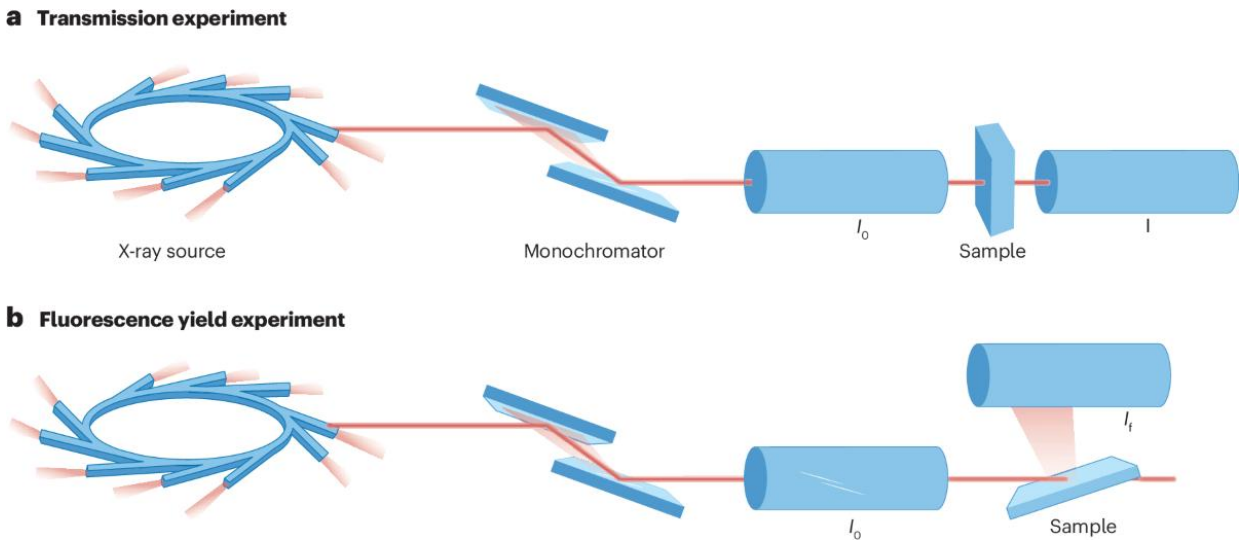
X-ray absorption spectroscopy

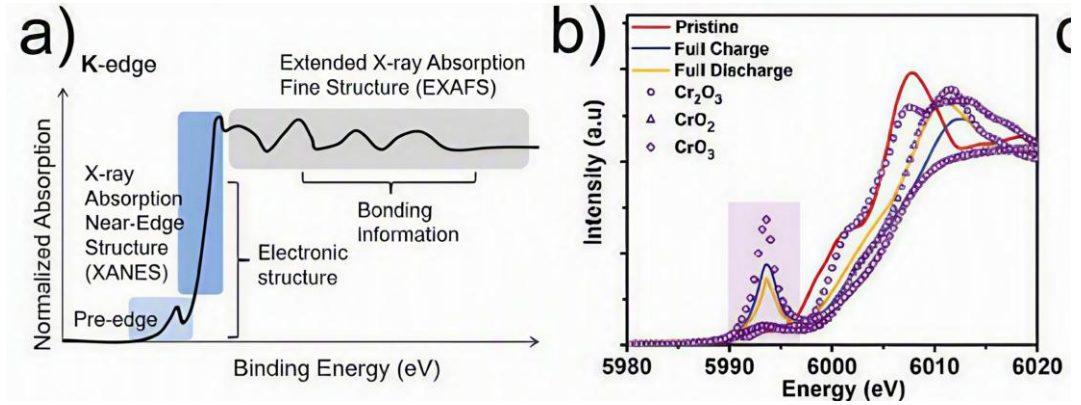
Synchrotron-based technique (mostly)

Can reveal the oxidation state and local bonding of a specific target element

Pros:
- Non-destructive* analysis
- Process tracking also in liquid, high T, etc

Cons:
- Limited accessibility
- Highly competitive
- Complex data analysis





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Overview

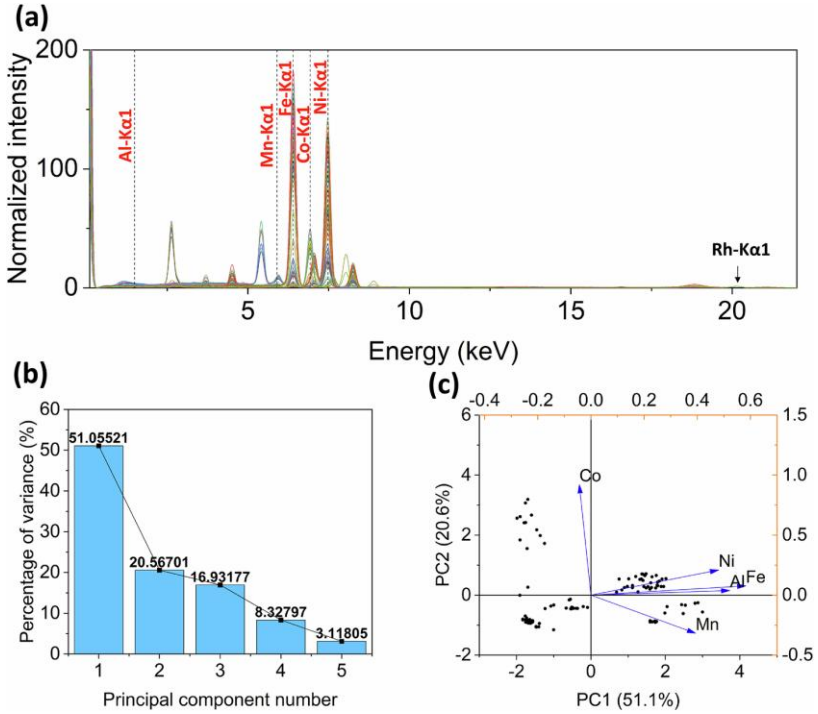
Technique	Bulk/surface	Detection limit	Spatial resolution	Portability	Speed	Cost
XRF	Bulk (µm - mm penetration)	Ppm - % (weak for light elements)	50 µm - mm	Handheld/field-portable	Fast (s – min)	Low-medium
ICP-OES	Bulk (destructive, solution)	Ppb – ppm	None (bulk digestion)	Lab only	Medium (min / sample)	Medium
ICP-MS	Bulk (destructive, solution)	Ppq – ppb	None (bulk digestion)	Lab only	Medium (min / sample)	High
LA-ICP-MS	Bulk+microspatial	Ppb – ppm	5 – 100 µm	Lab only	Medium	High
LIBS	Surface (µm depth/pulse)	Ppm - % (matrix dependent)	10 – 100 µm	Handheld/field-portable	Very fast (ms – sec)	Low-medium
SEM-EDX	Surface (µm depth)	0.1 – 1% (poor for light elements)	nm - µm	Lab only	Slow (min – h)	Medium-high
XPS	Surface (nm depth)	0.1 %	10 – 100 µm	Lab only	Slow (h)	High
XAS	Bulk (µm - mm penetration)	Ppm - % (matrix and detection dependent)	µm - mm	Lab only (synchrotron)	Variable	High

Rapid identification of cathode species in LIB by XRF

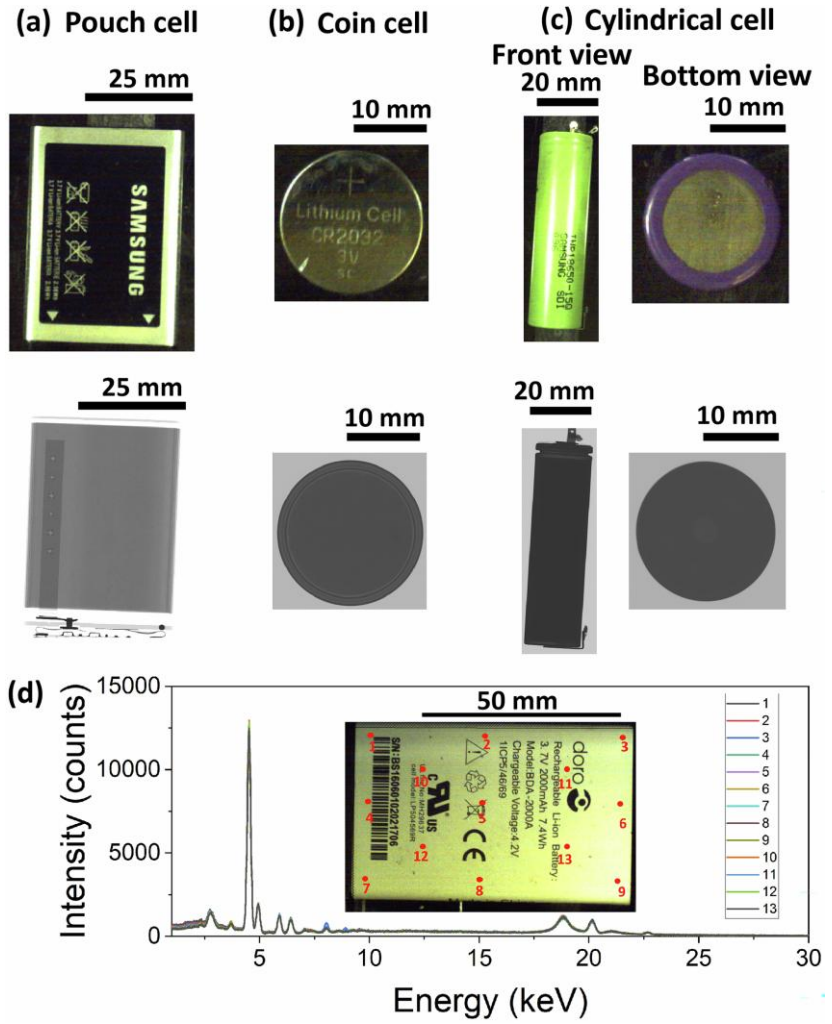
Cathode in LIB is rich in Co, Ni and Mn ($LiMn_2O_4$, $LiCoO_2$, $LiNi_xCo_yMn_zO_2$, $LiNi_xCo_yAl_zO_2$, and $LiFePO_4$)

Efficient sorting of EOL LIB prior to sorting improves recycling process

Most sorting process are destructive and/or impractical



Comm. Engin., 2026, 5, 67



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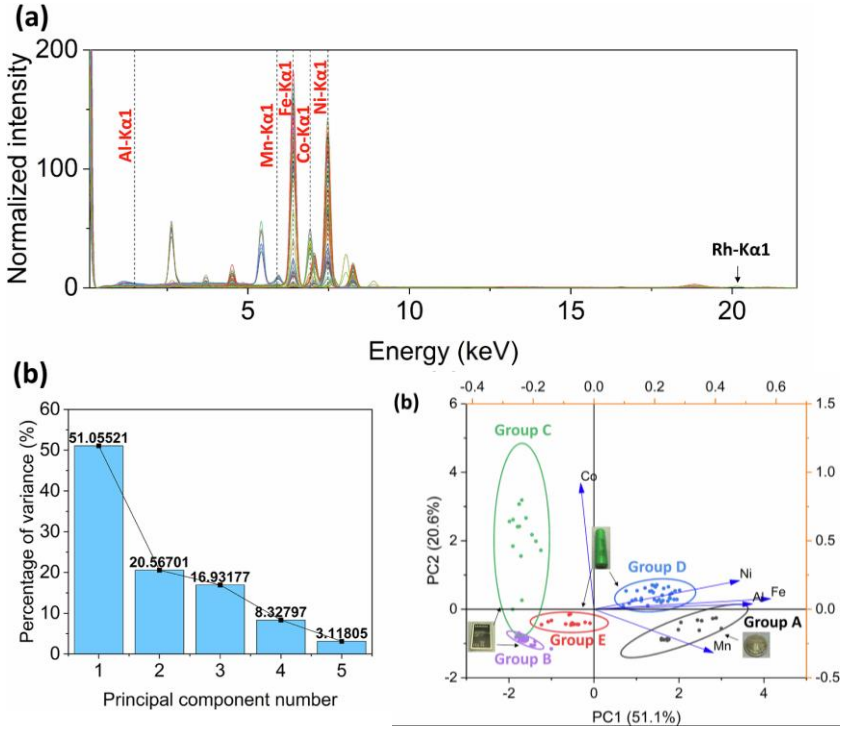
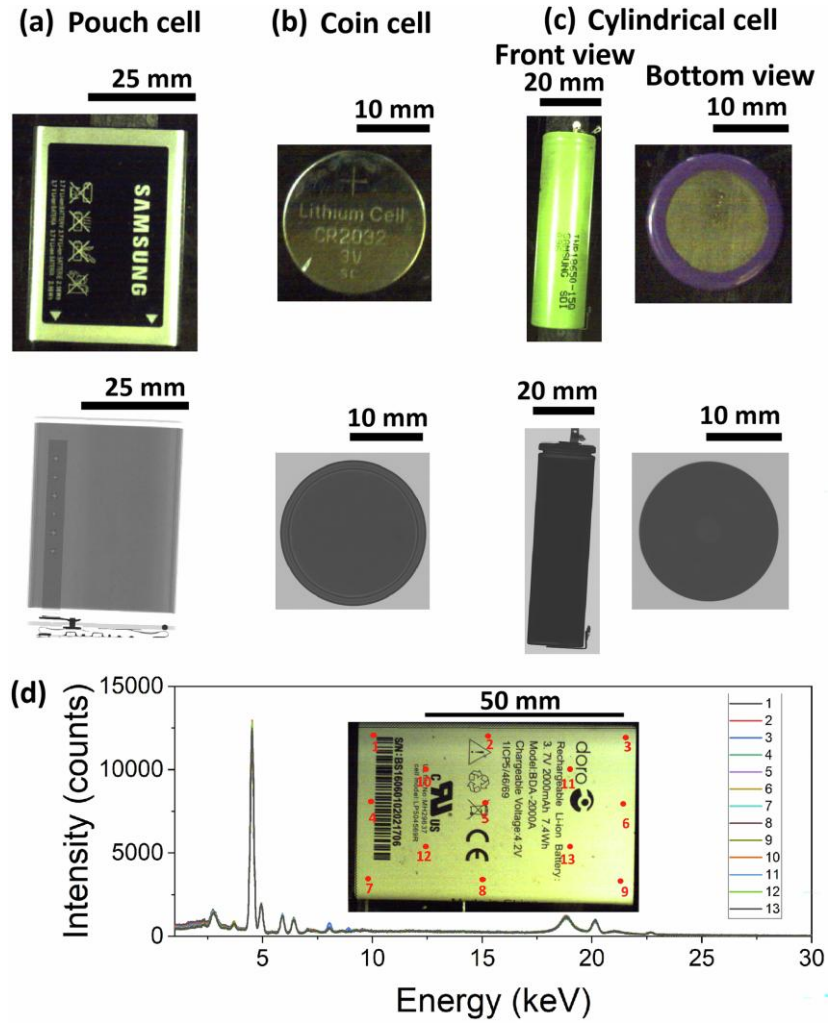


Comm. Engin., 2026, 5, 67



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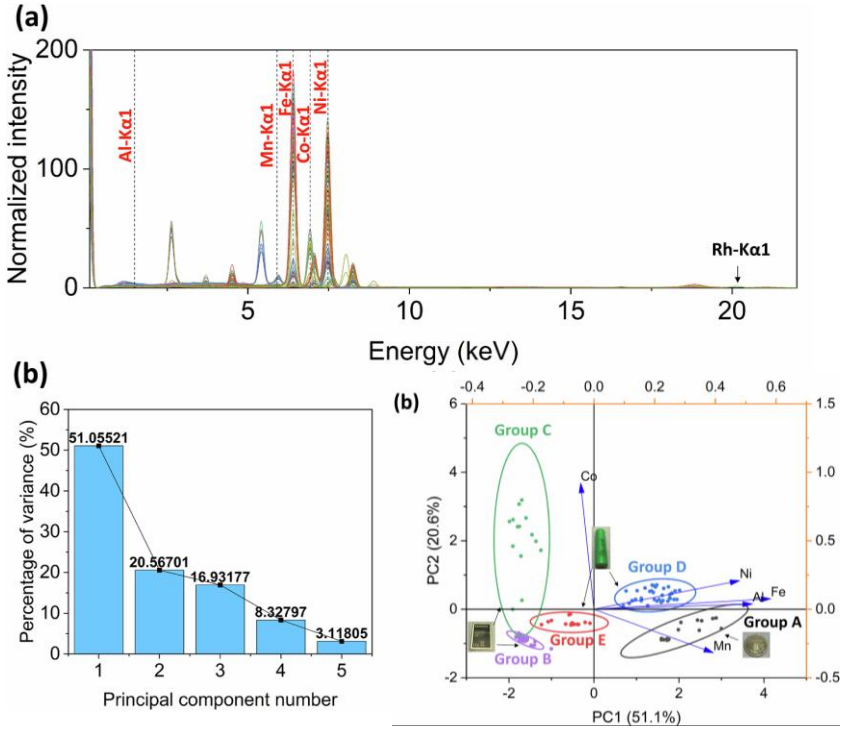
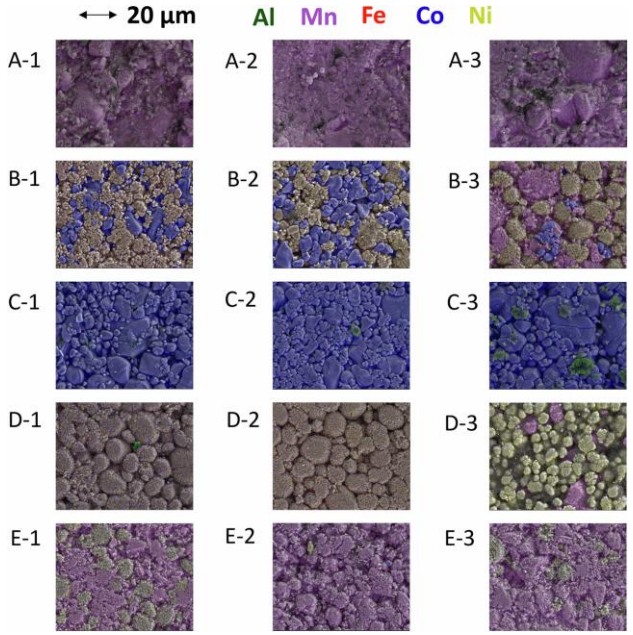
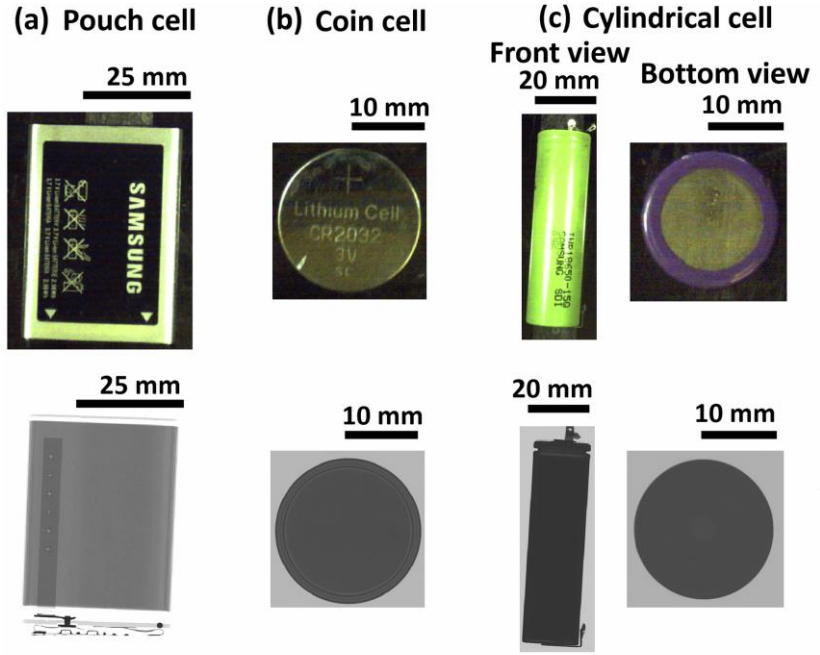
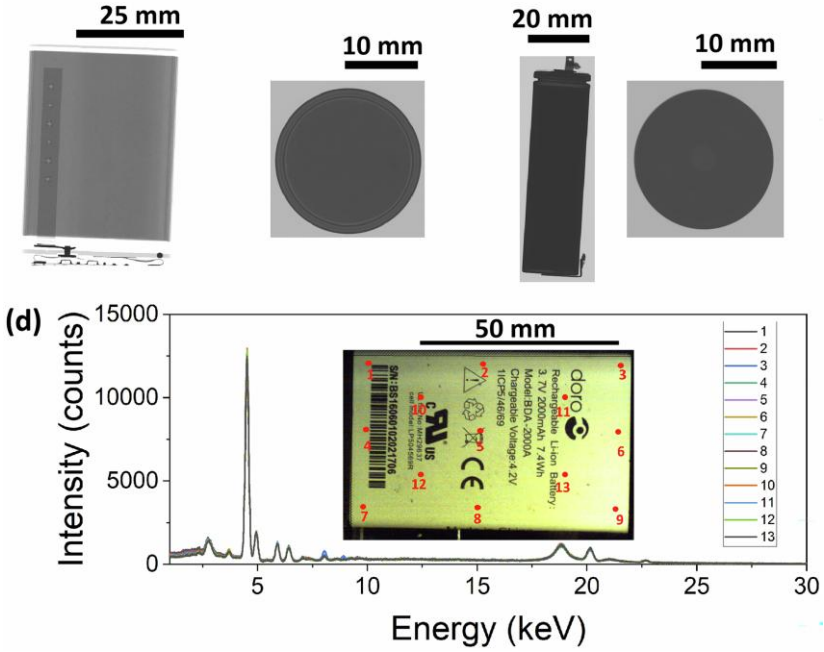








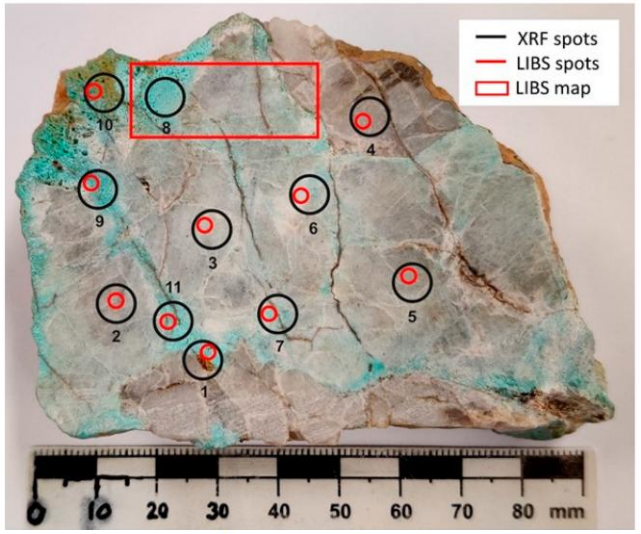
Comm. Engin., 2026, 5, 67

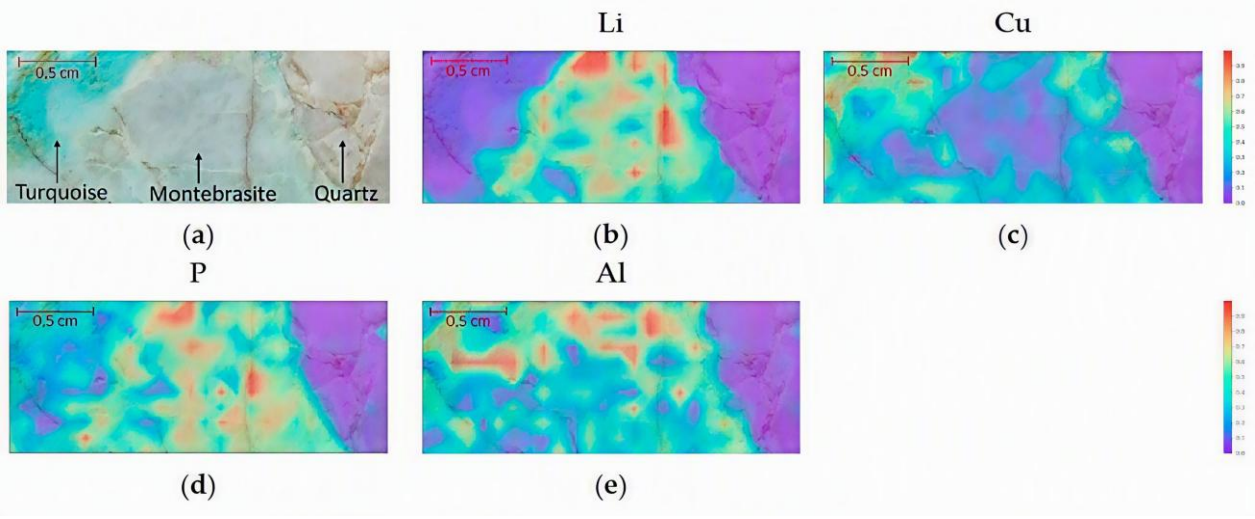
Analysis of Li-rich minerals from a Portuguese mine

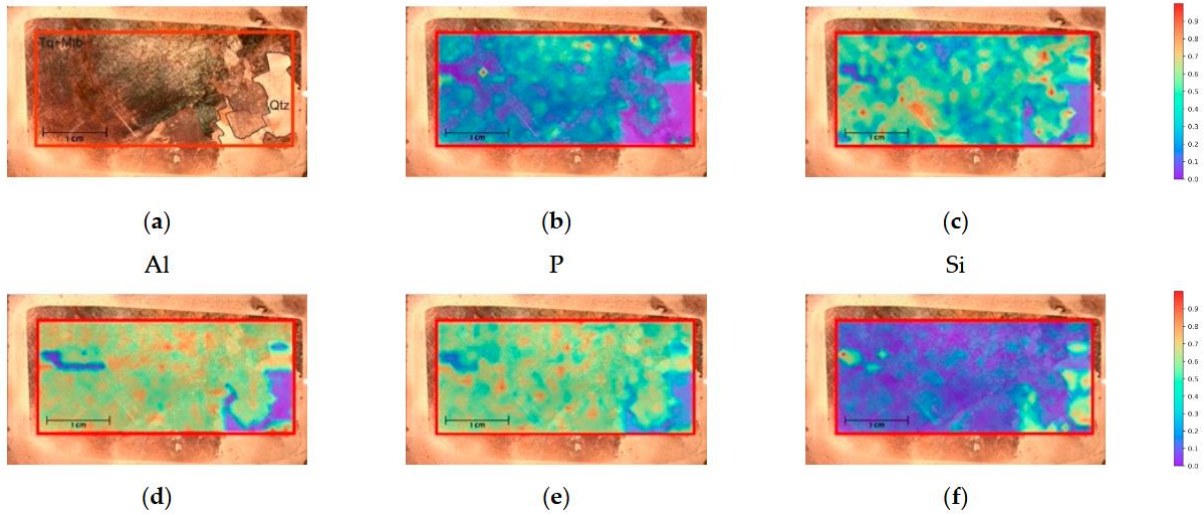
Assessment of possible Li-containing minerals in a mine sample

Co-presence of three different minerals (quartz, turquoise and montebrasite)

	Number of Measurements	Al_2O_3 (wt%)	Err (wt%)	SiO_2 (wt%)	Err (wt%)	K_2O (wt%)	Err (wt%)	Mn (wt%)	Err (wt%)	Fe (wt%)	Err (wt%)	Cu (wt%)	Err (wt%)	Rb (wt%)	Err (wt%)	Pb (wt%)	Err (wt%)
Measurements during the sample analysis	1	11.8	0.4	70.1	0.7	4.90	0.04	0.116	0.007	1.77	0.02	0.023	0.002	0.0149	0.0009	0.087	0.004
	2	11.6	0.4	69.0	0.7	4.83	0.04	0.119	0.007	1.80	0.02	0.022	0.002	0.0142	0.0009	0.093	0.004
	3	11.0	0.4	66.5	0.7	4.77	0.04	0.116	0.007	1.81	0.02	0.023	0.002	0.0147	0.0009	0.100	0.005
	4	11.4	0.4	66.8	0.7	4.71	0.04	0.118	0.007	1.79	0.02	0.023	0.002	0.0143	0.0009	0.095	0.005
	5	11.8	0.4	68.9	0.7	4.83	0.04	0.118	0.007	1.80	0.02	0.023	0.002	0.0142	0.0009	0.090	0.004
	6	11.4	0.4	67.0	0.7	4.75	0.04	0.113	0.007	1.76	0.02	0.022	0.002	0.0145	0.0009	0.098	0.005
	7	11.6	0.4	68.2	0.7	4.80	0.04	0.108	0.006	1.75	0.02	0.022	0.002	0.0144	0.0009	0.089	0.004
QC reference	Target Mean	11.82		68.79		4.78		0.110		1.75		0.0218		0.0142		0.0886	
	S. Deviation	0.19		1.00		0.08		0.003		0.01		0.0006		0.0004		0.0026	
	Limit MIN	10.89		63.82		4.36		0.095		1.70		0.0189		0.0122		0.0758	
	Limit MAX	12.74		73.77		5.19		0.126		1.80		0.0247		0.0162		0.1013	







Minerals., 2021, 11, 1169