Energy Dispersive X-Ray Fluorescence:

measuring elements in solid and liquid matrices

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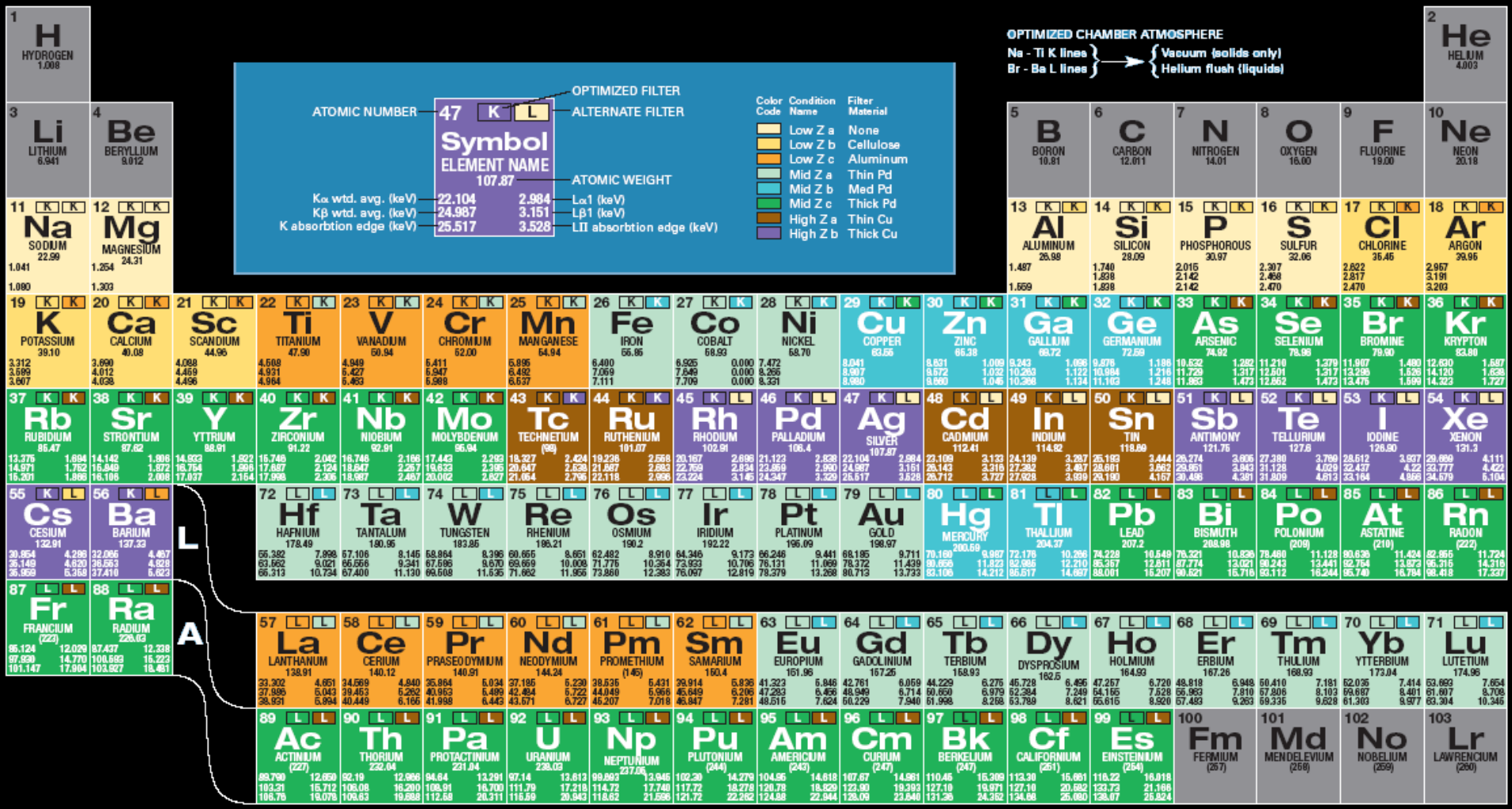
Outline

- Energy Dispersive X-Ray Fluorescence (EDXRF)
- Measurement Requirements
- Advantages and Disadvantages
- Analysis of Samples (I)
- Analysis of Samples (II)
- Analysis of Samples (III)
- Conclusions

Energy Dispersive X-Ray Fluorescence (EDXRF)

- Multi-element technique for solids, liquids, loose powders, etc.
- Up to 89 elements of the periodic table (from Na to Es)

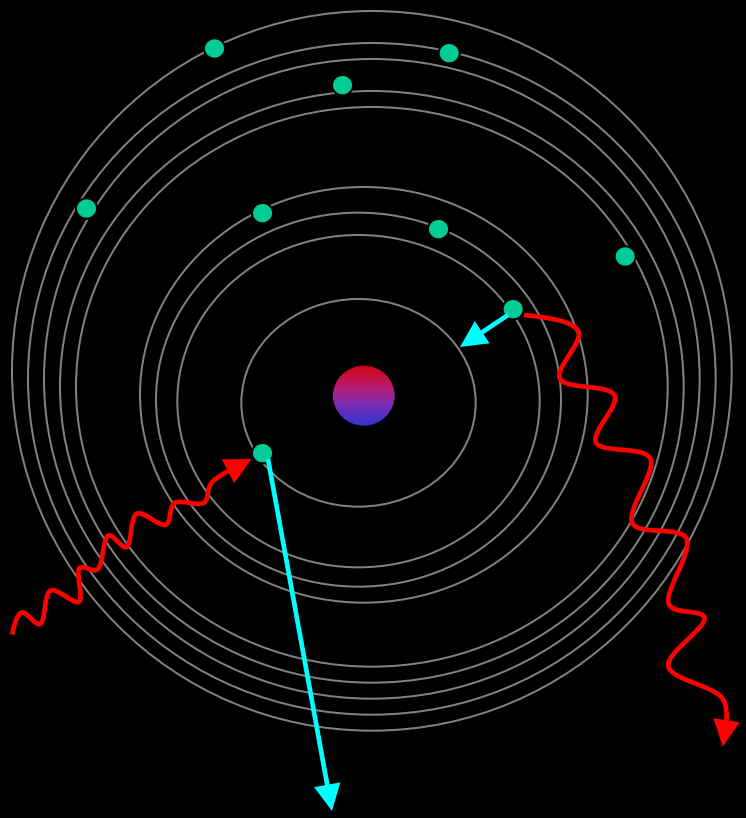


How is the X-ray signal produced?

- A source X-ray strikes an inner shell electron.

  If at high enough energy (above absorption edge of element), it is ejected it from the atom.

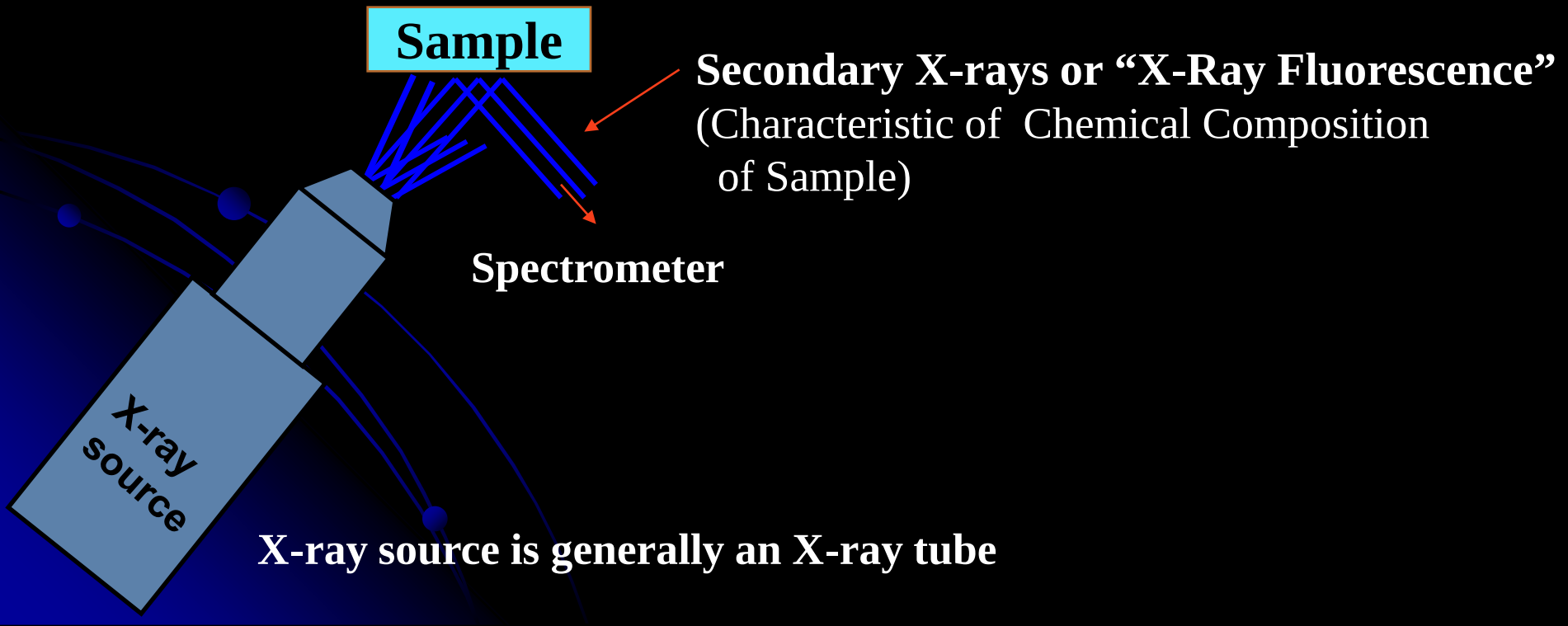
- Higher energy electrons cascade to fill vacancy, giving off characteristic fluorescent X-rays.



How does EDXRF works?

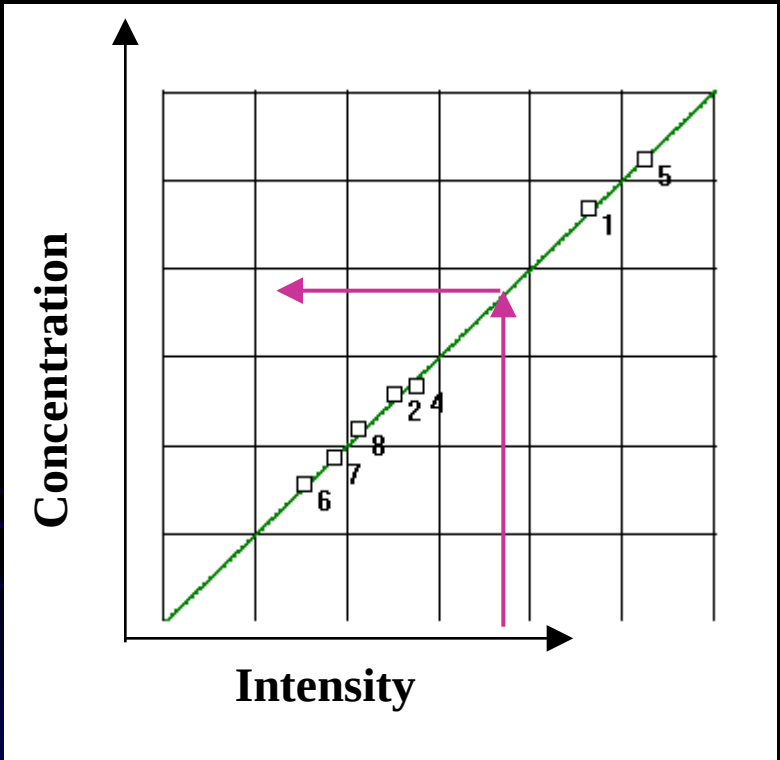
X-ray tube, sample excitation, detector

- Qualitative: wavelenght ↔ atomic number
- Quantitative: intensity ↔ concentration



X-ray source is generally an X-ray tube

Quantitative Analysis



- XRF is a reference method, standards are required for quantitative results
- Standards are analysed, intensities obtained, and a calibration plot is generated (intensities vs. concentration)
- XRF instruments compare the spectral intensities of unknown samples to those of known standards

Measurement Requirements

Chamber Atmosphere:

- **Air** (usually)

because air absorbs low energy x-rays → purges are often required

- The two most common purge methods are:
  - **Vacuum** → for use with solids or pressed pellets
  - **Helium** → for use with liquids or powdered materials

Advantages of X-Ray Fluorescence

- Simple spectra
- Spectral positions are almost independent of the chemical state of the analyte
- Minimal sample preparation
- It is non-destructive
- Applicable over a wide range of concentrations
- Good precision and accuracy
- Qualitative analysis can be performed in 50 s, or so
- Can be used to measure solid, powdered and liquid samples

Disadvantages of X-Ray Fluorescence

- X-ray penetration of the sample is limited to the top 0.01 - 0.1 mm layer
- Light elements (below Al) have very limited sensitivity although C is possible on new instruments
- Inter element (MATRIX) effects may be substantial and require computer correction
- Limits of detection are only modest
- Instrumentation is fairly expensive

Analysis of Samples (I)

Powder

Received Sample	SIS Sample
Purpose	Determine unknown components (qualitative and quantitative)
Sample preparation	Not required
Analysis technique	Intensity correction (quantitative analysis)

Analytical Conditions used to analyse SIS sample

- **Condition Name: Low Za → Detected elements: Mg, Al, Si, P**

Voltage	4 kV	Current	Auto
Livetime	50 seconds	Counts Limit	0
Filter	No Filter	Atmosphere	Helium
Maximum Energy:	10 keV	Count Rate	Medium

- **Condition Name: Mid Za → Detected elements: Ni, Fe**

Voltage:	14 kV	Current	Auto
Livetime:	50 seconds	Counts Limit	0
Filter:	Pd Thin	Atmosphere	Air
Maximum Energy:	20 keV	Count Rate	Medium

Analytical Conditions used to analyse SIS sample (continued)

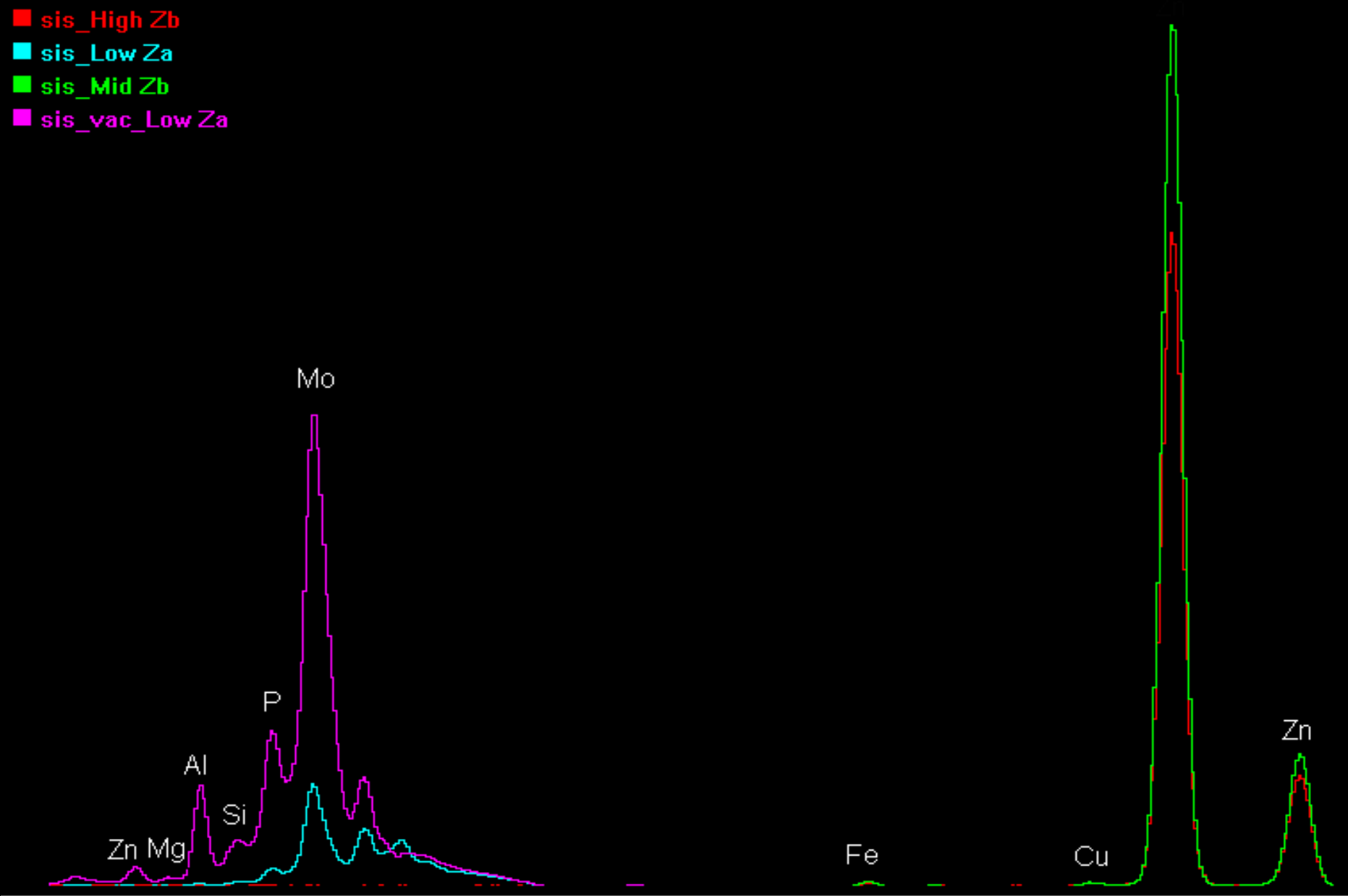
- **Condition Name: Mid Zb → Detected elements: Cu, Zn**

Voltage	15 kV ; 17 kV	Current	Auto
Livetime	50 seconds	Counts Limit	0
Filter	Pd Medium	Atmosphere	Air
Maximum Energy:	20 keV	Count Rate	Medium

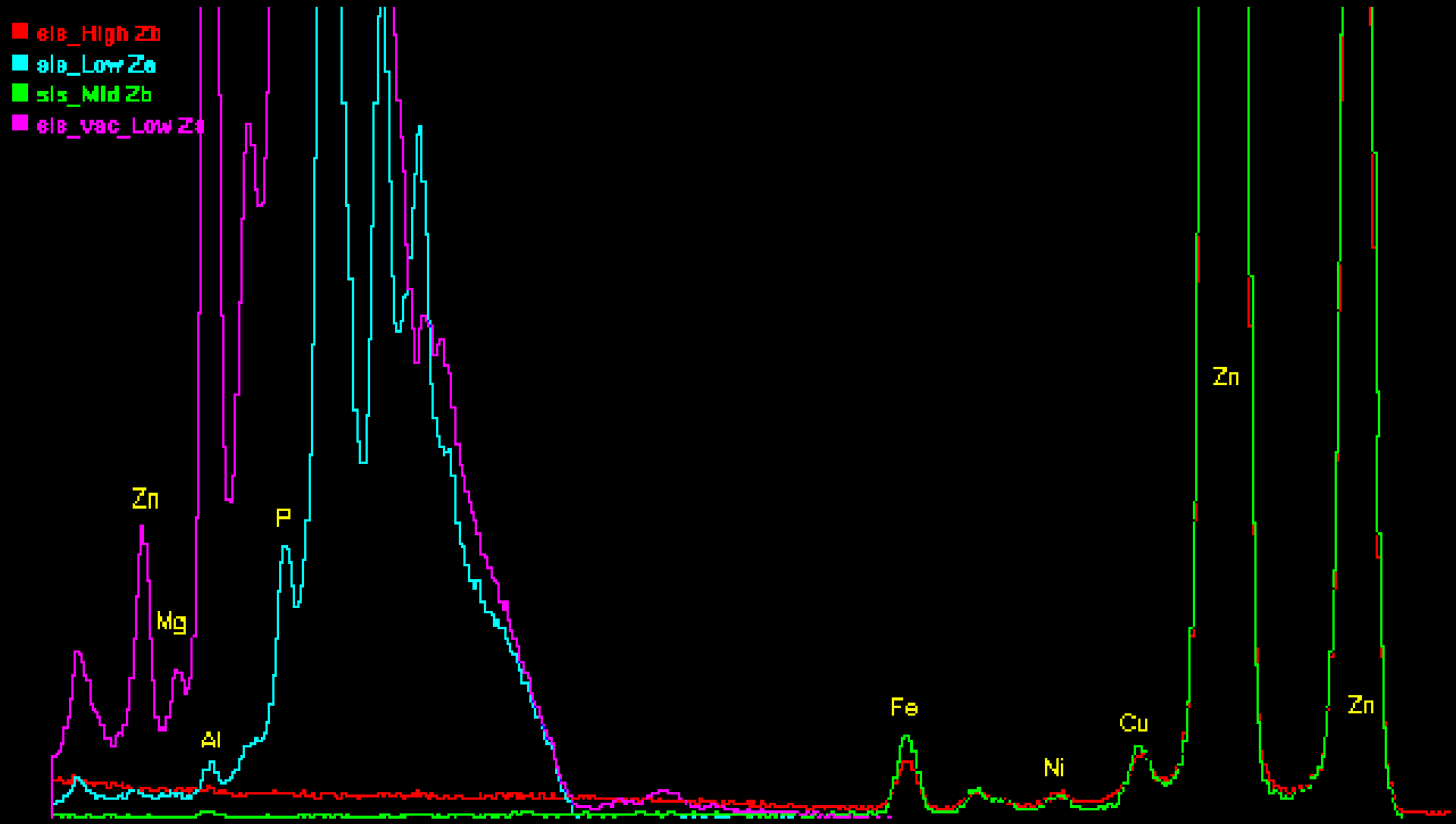
- **Condition Name: Mid Zc → Detected elements: Mo**

Voltage:	35 kV	Current	Auto
Livetime:	50 seconds	Counts Limit	0
Filter:	Pd Thick	Atmosphere	Air
Maximum Energy:	40 keV	Count Rate	Medium

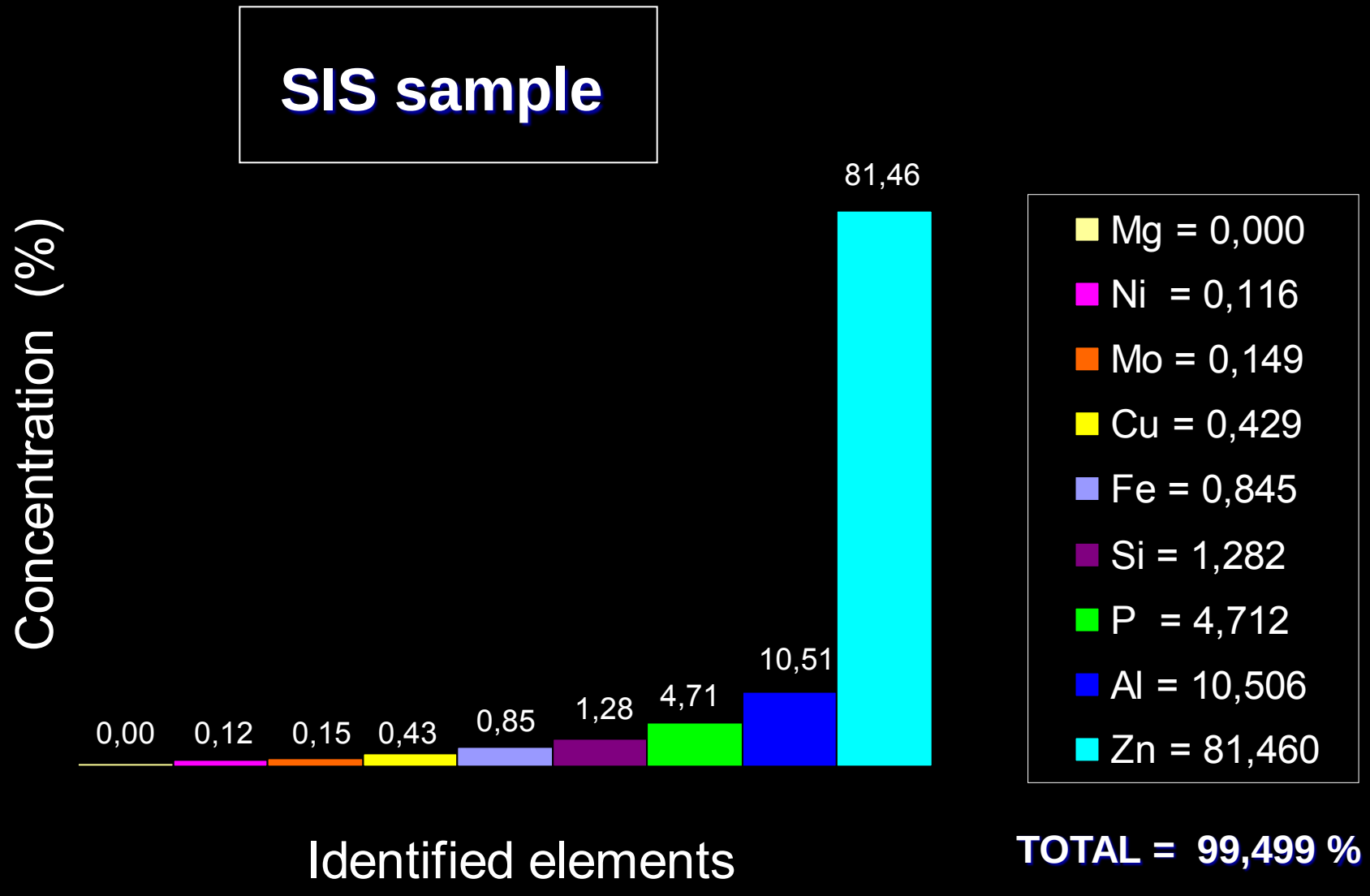
Overlap spectrum obtained



Overlap spectrum enlarged



Powder sample analysis results



TOTAL = 99,499 %

Conclusions

- The analysis performed was quite good, because the total sum is nearly 100 %
- Mg = 0,00 % is maybe because the calibration line for Mg was not adjusted properly.

Analysis of Samples (II)

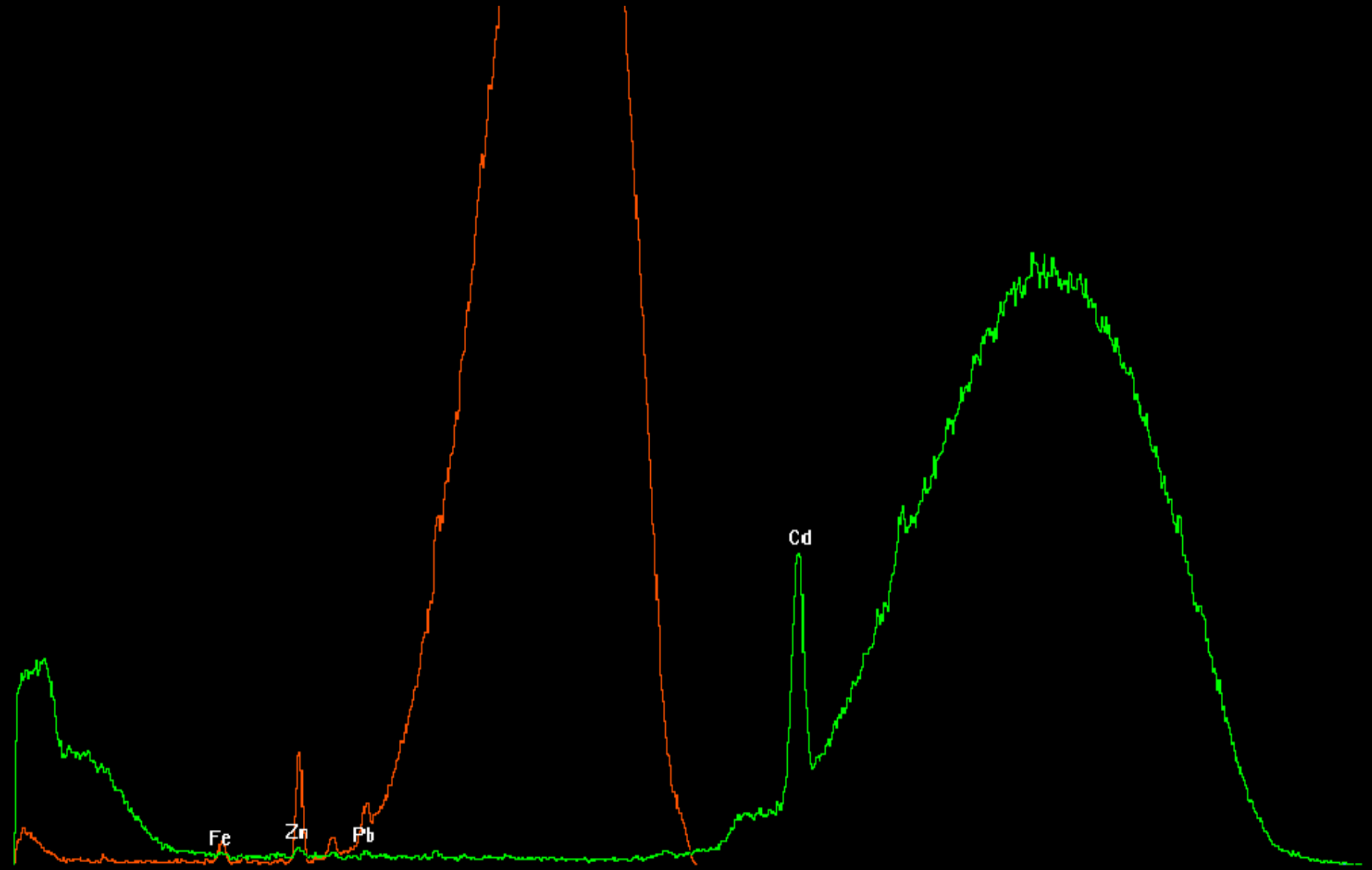
Liquid

Sample	Nitrates dissolved in water
Purpose	Determine detection limits of heavy metals in water
Sample preparation	Dissolutions prepared from Stock Solution 1,057 M
Analysis technique	Qualitative analysis

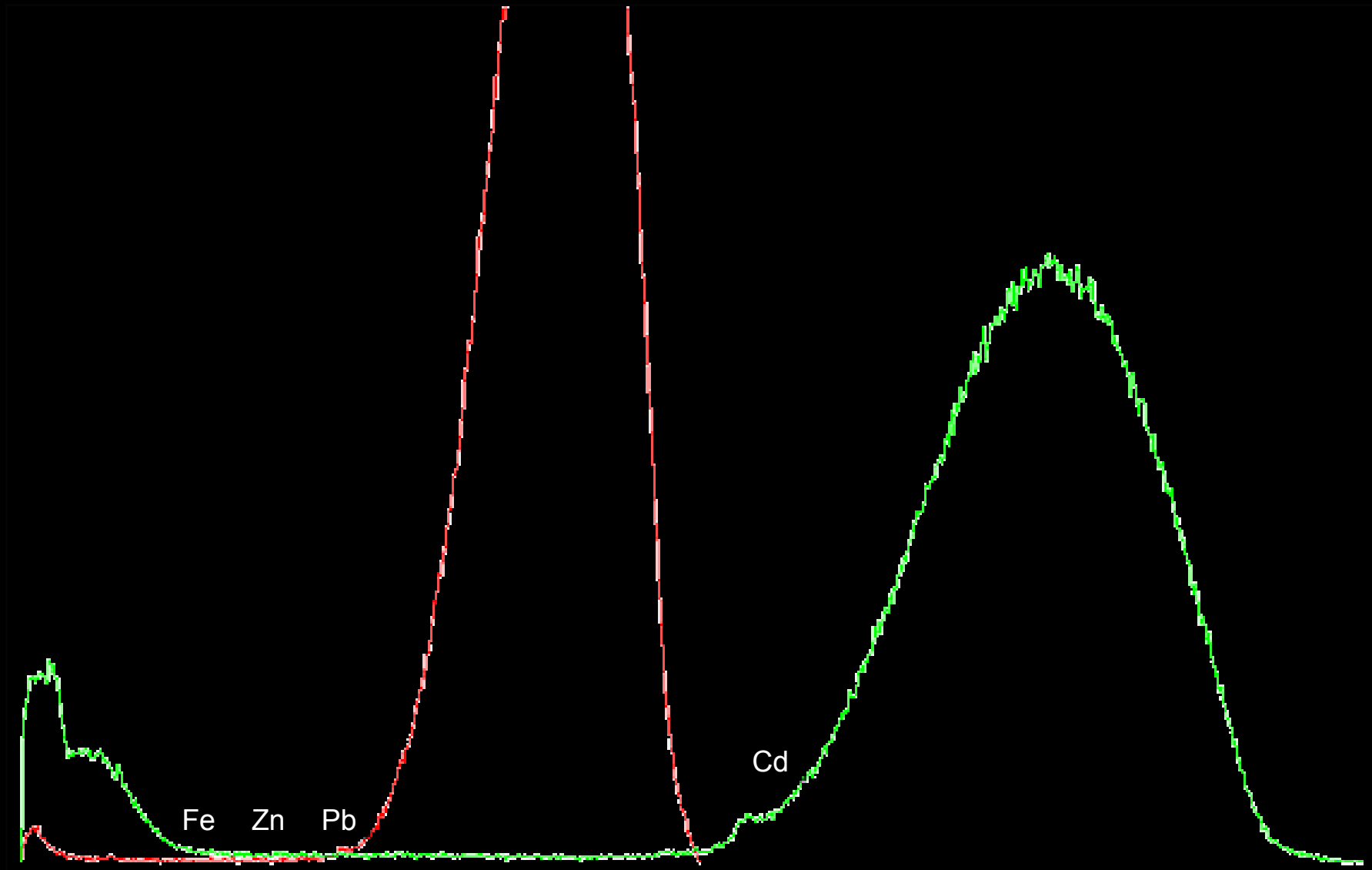
Liquid sample analysis results

Solution	ppm compound	✓ = detected	X = not detected
“A”	29.516,73 ppm Fe	✓	
	34.553,33 ppm Zn	✓	
	59.408,69 ppm Cd	✓	
	109.505,20 ppm Pb	✓	
“B”	2.951,67 ppm Fe	✓	
	3.455,33 ppm Zn	✓	
	5.940,87 ppm Cd	✓	
	10.950,52 ppm Pb	✓	
“C”	295,11 ppm Fe	✓	
	345,53 ppm Zn	✓	
	594,09 ppm Cd	✓	
	1095,05 ppm Pb	✓	
“D”	29,52 ppm Fe	✓	
	34,55 ppm Zn	✓	
	59,41 ppm Cd		X
	109,51 ppm Pb		X
“E”	2,95 ppm Fe		X
	3,45 ppm Zn		X
	5,94 ppm Cd		X
	10,95 ppm Pb		X

Resulting spectra with all the compounds detected



Resulting spectra with no compounds detected



Conclusions

- Concentrations > 100 ppm → peaks appear clearly
- Between 10 – 100 ppm → limit of detection (critical zone)
- Concentrations < 10 ppm → any peaks appearing

Analysis of Samples (III)

Oil

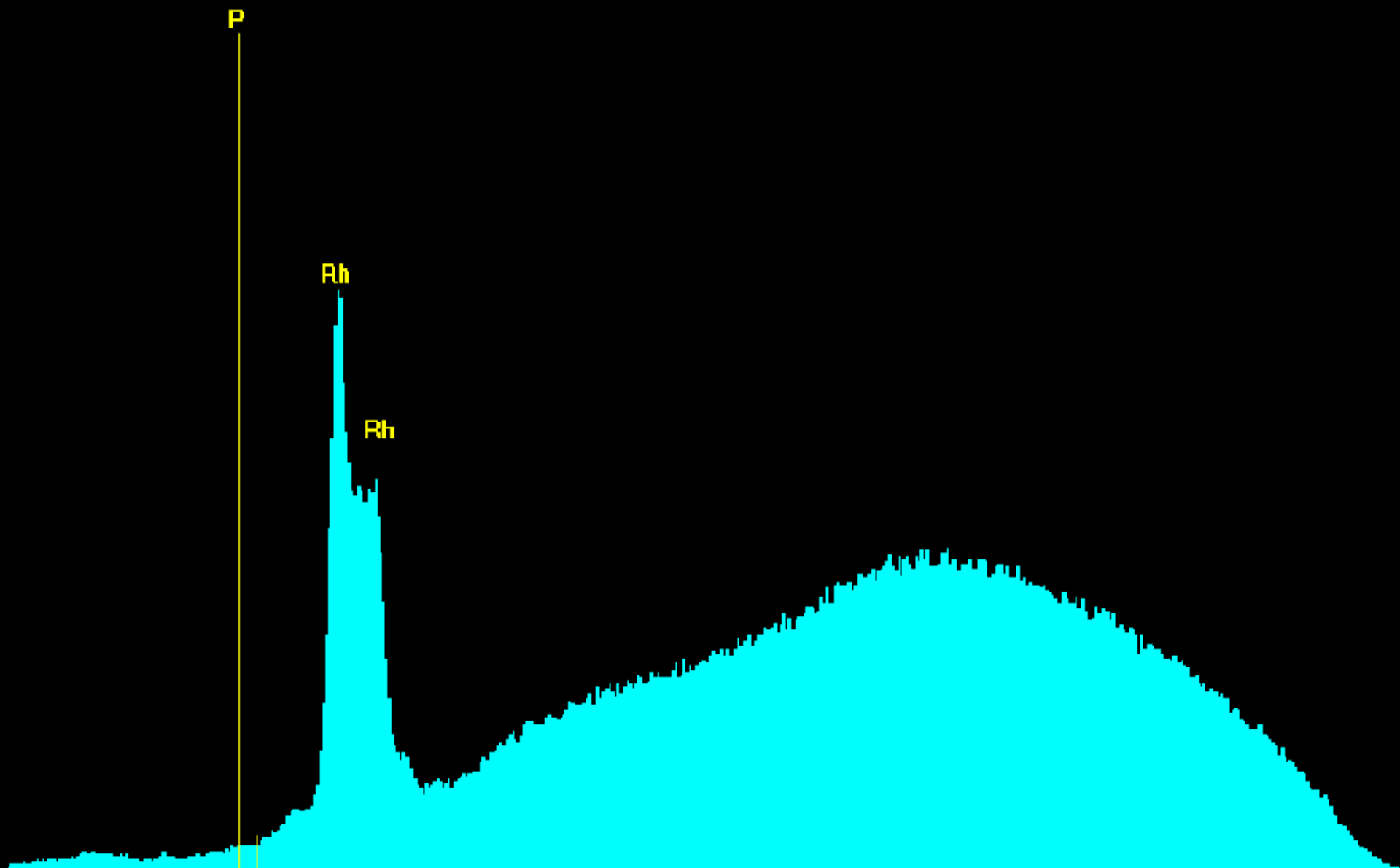
- Qualitative measurement of sunflower-oil and bolecht (lecithin)
- Detection limit for P by adding bolecht to sunflower oil

- Qualitative measurements of sunflower-oil and lecithin

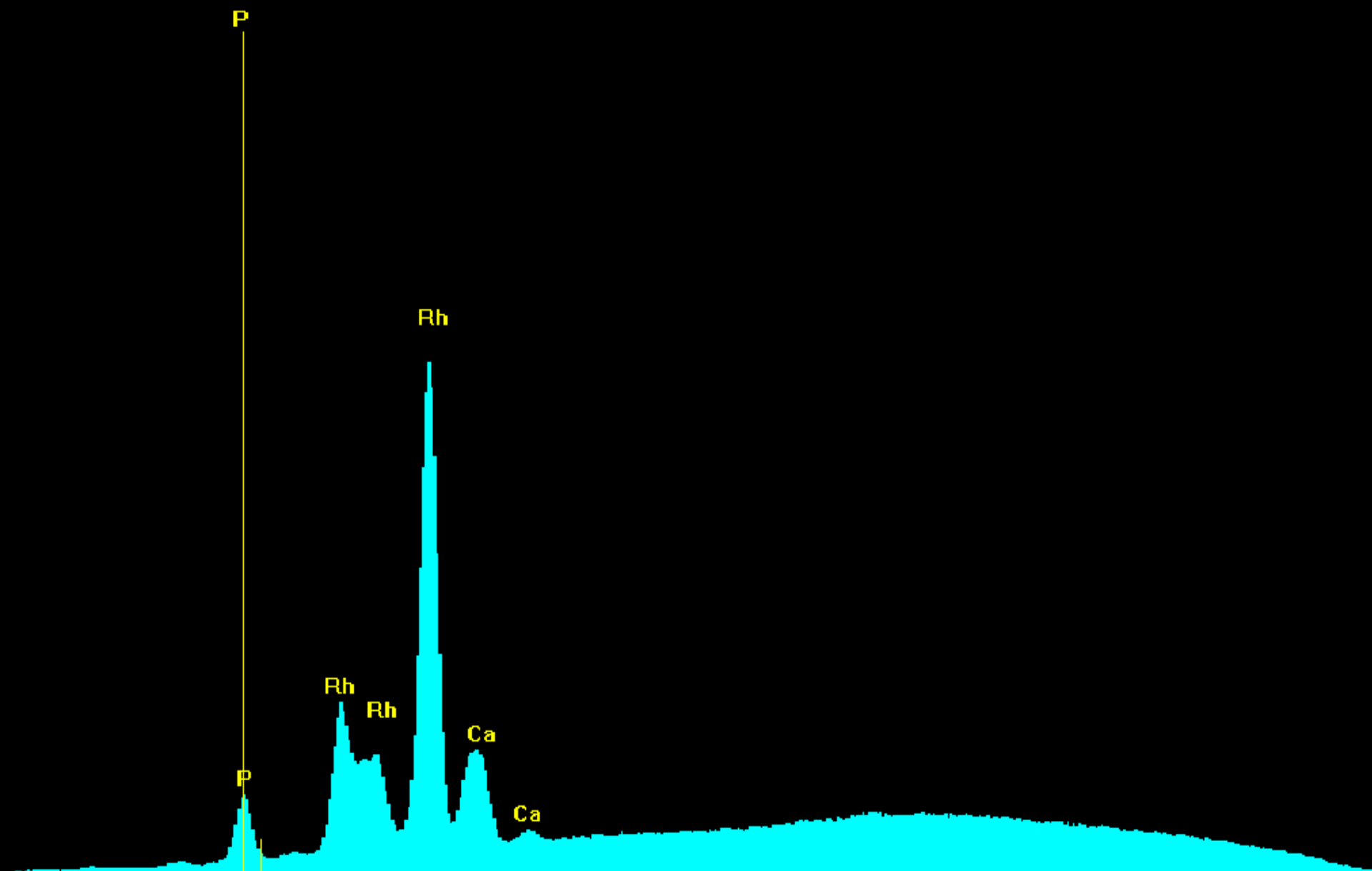
Conditions used :

Condition name	Low Za
Filter	No filter
Voltage	4 kV
Atmosphere	**Air**
Analyzed element	P
Count Rate	Medium
Live Time	100 sec

Spectrum obtained performing qualitative analysis of sunflower oil



Spectrum obtained performing qualitative analysis of bolecht (lecithin)



- Detection limit for P by adding bolecht to sunflower oil

MEASUREMENT		SPECTRA OBTAINED
0,46 % (w/w) lecithin	→	no P peak
1,00 % (w/w) lecithin	→	apparently a very small P peak
2,00 % (w/w) lecithin	→	clear P peak
5,00 % (w/w) lecithin	→	very clear P peak

Conclusions

- In concentrations lower than 10 ppm, phosphorus is almost impossible to detect.
- When concentrations are higher than 15 ppm, phosphorus is detected clearly.

THANK YOU FOR YOUR ATTENTION !