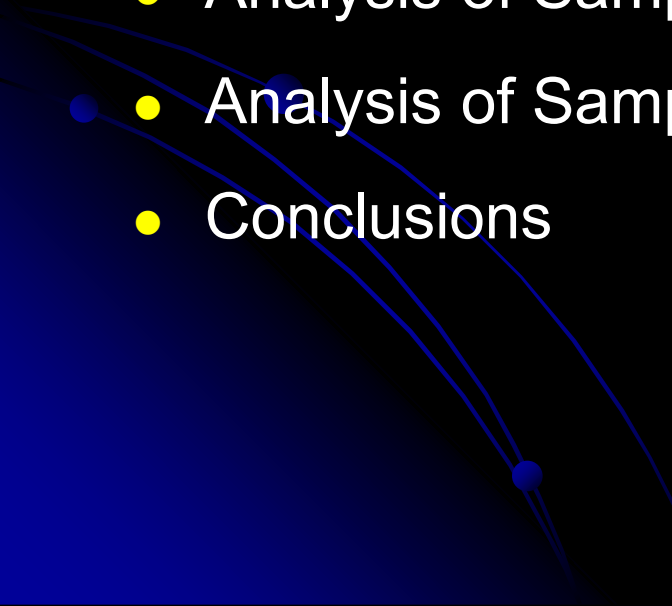


Energy Dispersive X-Ray Fluorescence: measuring elements in solid and liquid matrices

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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)

OPTIMIZED CHAMBER ATMOSPHERE

Na - Ti K lines } Vacuum (solids only)
 Br - Ba L lines } Helium flush (liquids)

ATOMIC NUMBER 47 **K** **L** OPTIMIZED FILTER
 ALTERNATE FILTER

Color Code Condition Name Filter Material

- Low Z a None
- Low Z b Cellulose
- Low Z c Aluminum
- Mid Z b Thin Pd
- Mid Z c Med Pd
- Mid Z c Thick Pd
- High Z a Thin Cu
- High Z b Thick Cu

Symbol **K** **L**
 ELEMENT NAME
 107.87 ATOMIC WEIGHT

K α wtd. avg. (keV) 22.104 2.984
 K β wtd. avg. (keV) 24.987 3.151
 K absorption edge (keV) 25.517 3.528

L α 1 (keV)
 L β 1 (keV)
 L γ 1 absorption edge (keV)

5 B BORON 10.81	6 C CARBON 12.01	7 N NITROGEN 14.01	8 O OXYGEN 16.00	9 F FLUORINE 19.00	10 Ne NEON 20.18
13 Al ALUMINUM 26.98	14 Si SILICON 28.09	15 P PHOSPHORUS 30.97	16 S SULFUR 32.06	17 Cl CHLORINE 35.45	18 Ar ARGON 39.96

19 K POTASSIUM 39.10	20 Ca CALCIUM 40.08	21 Sc SCANDIUM 44.96	22 Ti TITANIUM 47.88	23 V VANADIUM 50.94	24 Cr CHROMIUM 52.00	25 Mn MANGANESE 54.94	26 Fe IRON 55.85	27 Co COBALT 58.93	28 Ni NICKEL 58.70	29 Cu COPPER 63.55	30 Zn ZINC 65.38	31 Ga GALLIUM 69.72	32 Ge GERMANIUM 72.63	33 As ARSENIC 74.92	34 Se SELENIUM 78.96	35 Br BROMINE 79.90	36 Kr KRYPTON 83.80
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37 Rb RUBIDIUM 85.47	38 Sr STRONTIUM 87.62	39 Y YTTORIUM 88.91	40 Zr ZIRCONIUM 91.22	41 Nb NIOBIUM 92.91	42 Mo MOLYBDENUM 95.94	43 Tc TECHNETIUM (99)	44 Ru RUTHENIUM 101.07	45 Rh RHODIUM 102.91	46 Pd PALLADIUM 106.4	47 Ag SILVER 107.87	48 Cd CADMIUM 112.41	49 In INDIUM 114.82	50 Sn TIN 118.59	51 Sb ANTIMONY 121.75	52 Te TELLURIUM 127.6	53 I IODINE 126.90	54 Xe XENON 131.3
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55 Cs CESIUM 132.91	56 Ba BARIUM 137.33	57 La LANTHANUM 138.91	58 Ce CERIUM 140.12	59 Pr PRASEODYMIUM 140.91	60 Nd NEODYMIUM 144.24	61 Pm PROMETHIUM (145)	62 Sm SAMARIUM 150.4	63 Eu EUROPIUM 151.96	64 Gd GADOLINIUM 157.25	65 Tb TERBIUM 158.93	66 Dy DYSPROSIUM 162.5	67 Ho HOLMIUM 164.93	68 Er ERBIUM 167.26	69 Tm THULIUM 168.93	70 Yb YTTERIUM 173.04	71 Lu LUTETIUM 174.96
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11 Na SODIUM 22.99	12 Mg MAGNESIUM 24.31	13 Al ALUMINUM 26.98	14 Si SILICON 28.09	15 P PHOSPHORUS 30.97	16 S SULFUR 32.06	17 Cl CHLORINE 35.45	18 Ar ARGON 39.96
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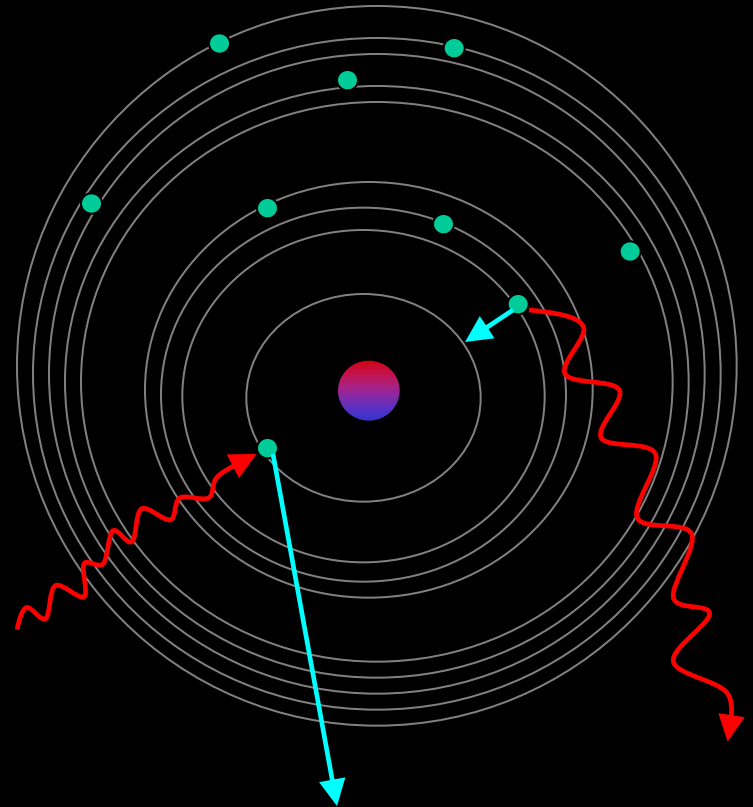
72 Hf HAFNIUM 178.49	73 Ta TANTALUM 180.95	74 W WOLFRAM 183.85	75 Re RHENIUM 186.21	76 Os OSMIUM 190.2	77 Ir IRIDIUM 192.22	78 Pt PLATINUM 195.08	79 Au GOLD 196.97	80 Hg MERCURY 200.59	81 Tl THALLIUM 204.37	82 Pb LEAD 207.2	83 Bi BISMUTH 208.98	84 Po POLONIUM (209)	85 At ASTATINE (210)	86 Rn RADON (222)
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87 Fr FRANCIUM (223)	88 Ra RADIUM 226.02	89 Ac ACTINIUM (227)	90 Th THORIUM 232.04	91 Pa PROTACTINIUM 231.04	92 U URANIUM 238.03	93 Np NEPTUNIUM 237.05	94 Pu PLUTONIUM (244)	95 Am AMERICIUM (243)	96 Cm CURIUM (247)	97 Bk BERKELIUM (247)	98 Cf CALIFORNIUM (251)	99 Es EINSTEINIUM (254)	100 Fm FERMIUM (257)	101 Md MENDELEVIUM (258)	102 No NOBELIUM (259)	103 Lr LAWRENCIUM (260)
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1 H HYDROGEN 1.008	2 He HELIUM 4.003
3 Li LITHIUM 6.941	4 Be BERYLLIUM 9.012
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69 Tm THULIUM 168.93	70 Yb YTTERIUM 173.04
71 Lu LUTETIUM 174.96	

How is the X-ray signal produced?

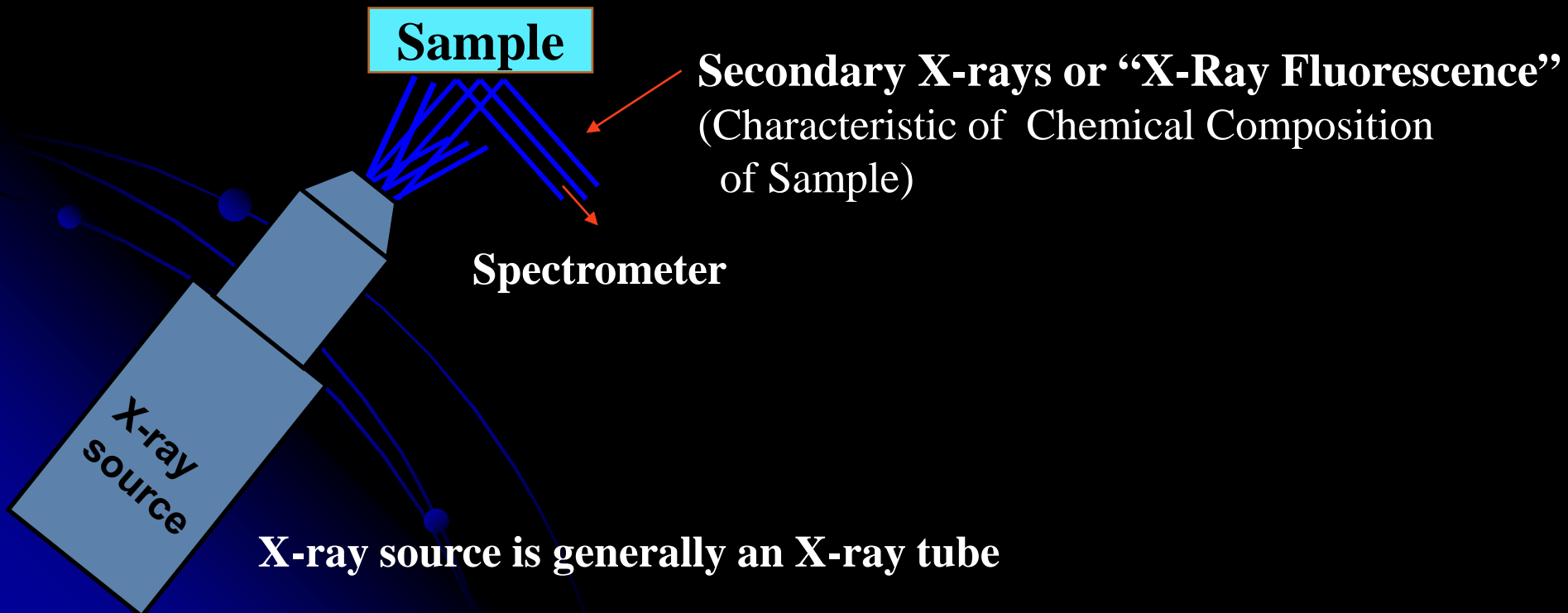
- A source X-ray strikes an inner shell electron. If at high enough energy (above absorption edge of element), it is ejected from the atom.
- Higher energy electrons cascade to fill vacancy, giving off characteristic fluorescent X-rays.



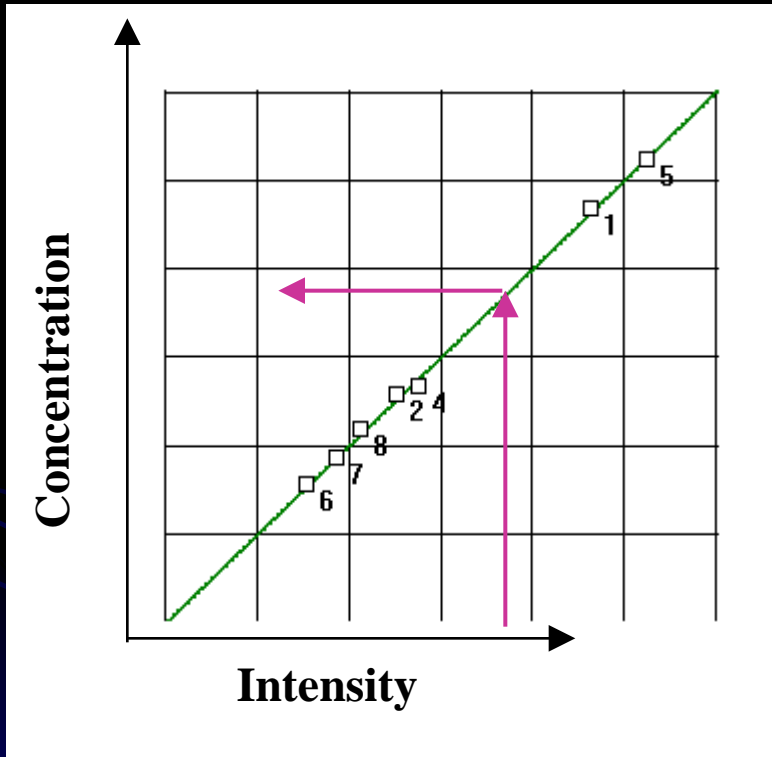
How does EDXRF works?

X-ray tube, sample excitation, detector

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



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

<u>Received Sample</u>	SIS Sample
<u>Purpose</u>	Determine unknown components (qualitative and quantitative)
<u>Sample preparation</u>	Not required
<u>Analysis technique</u>	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**

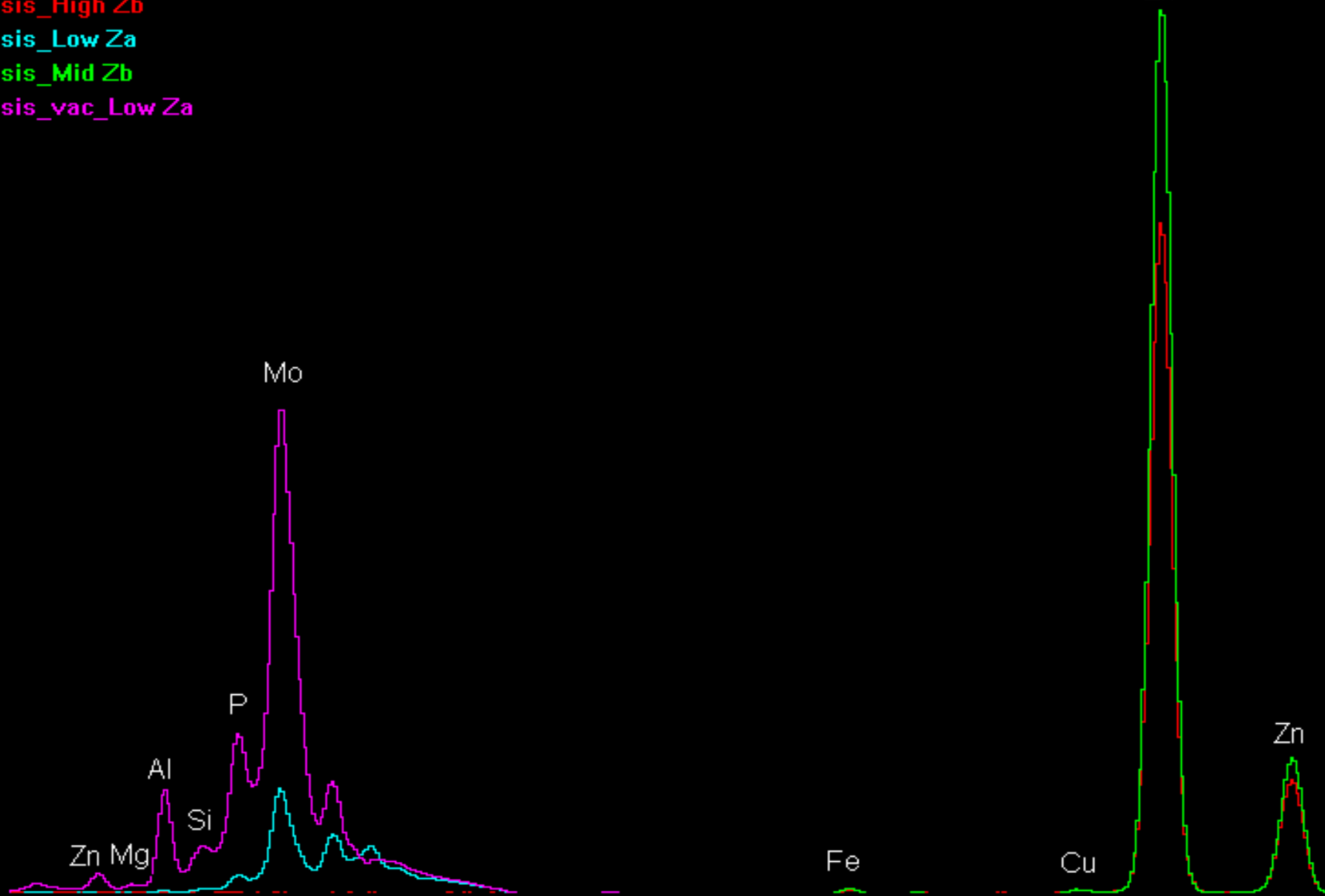
Voltage	15 kV ; 17 kV	Current	Auto
Livetime	50 seconds	Counts Limit	0
Filter	Pd Medium	Atmosphere	Air
Maximum Energy:	20 keV	Count Rate	Medium

- **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

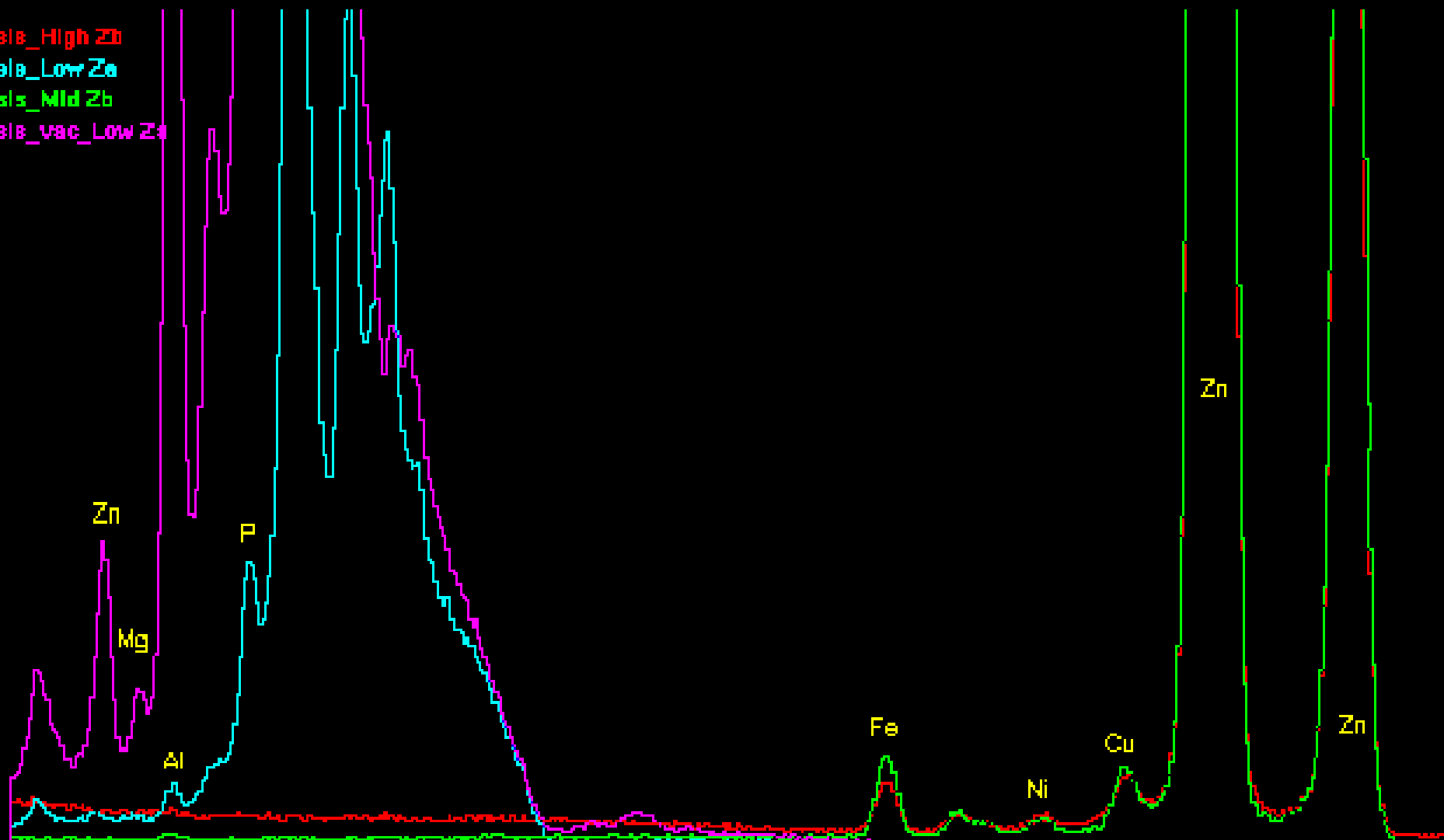
Overlap spectrum obtained

- sis_High Zb
- sis_Low Za
- sis_Mid Zb
- sis_vac_Low Za



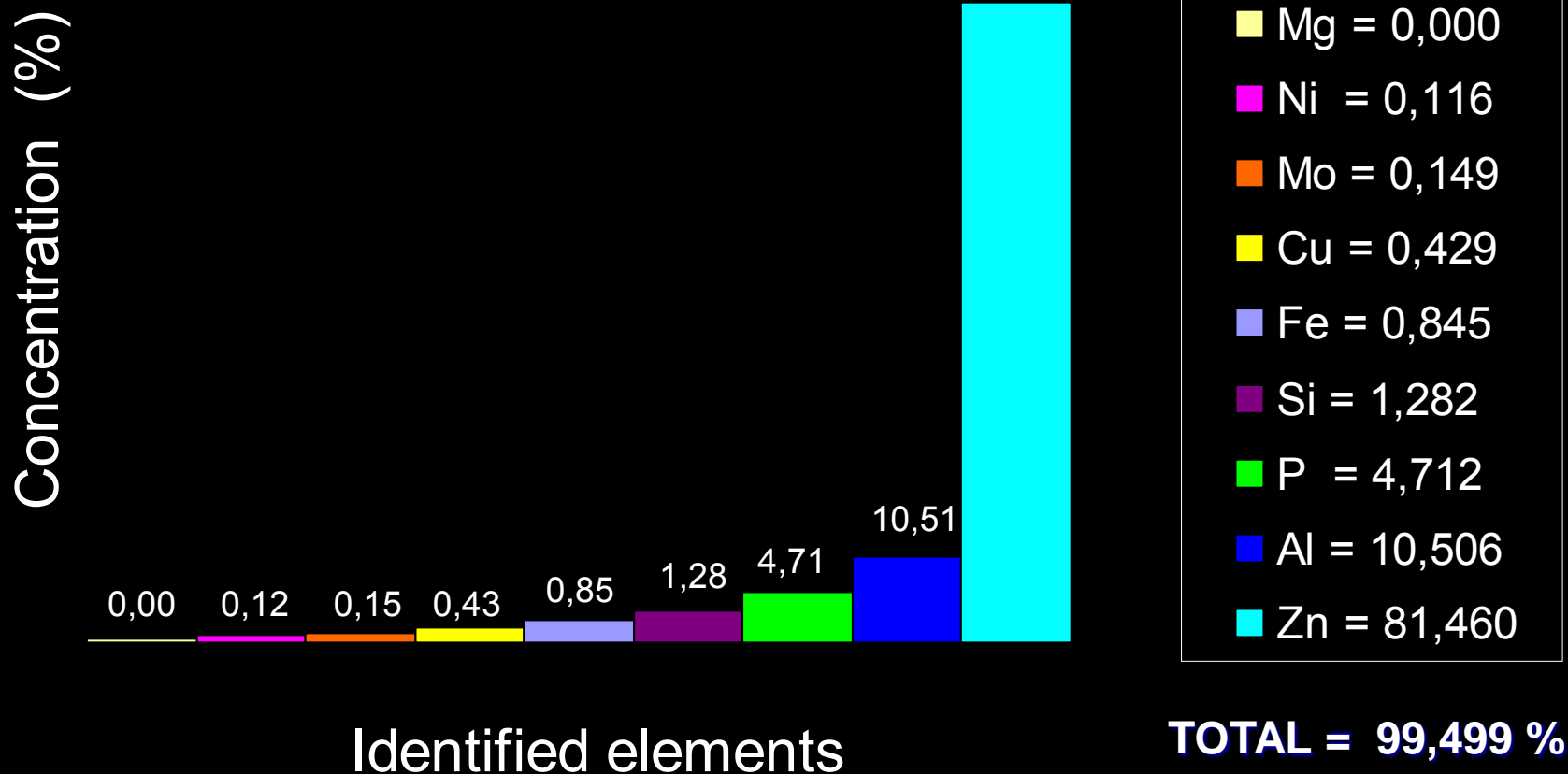
Overlap spectrum enlarged

- ele_High Zb
- ele_Low Za
- ele_Mid Zb
- ele_vac_Low Za



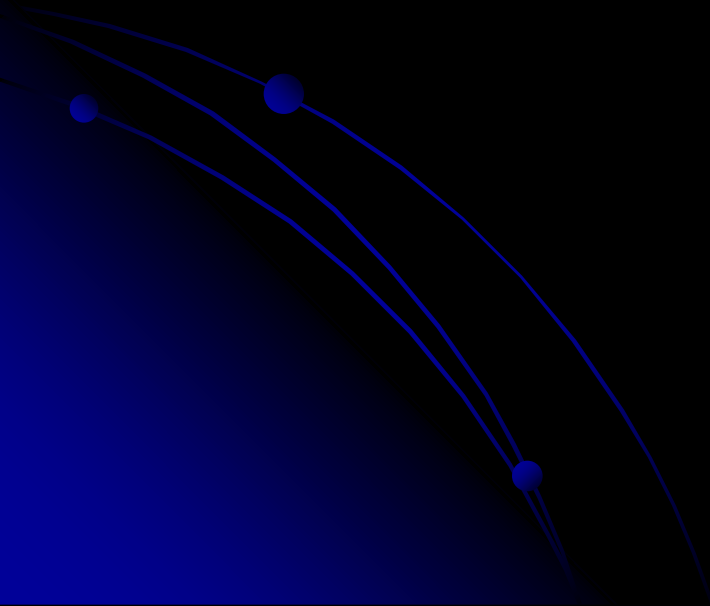
Powder sample analysis results

SIS sample



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)

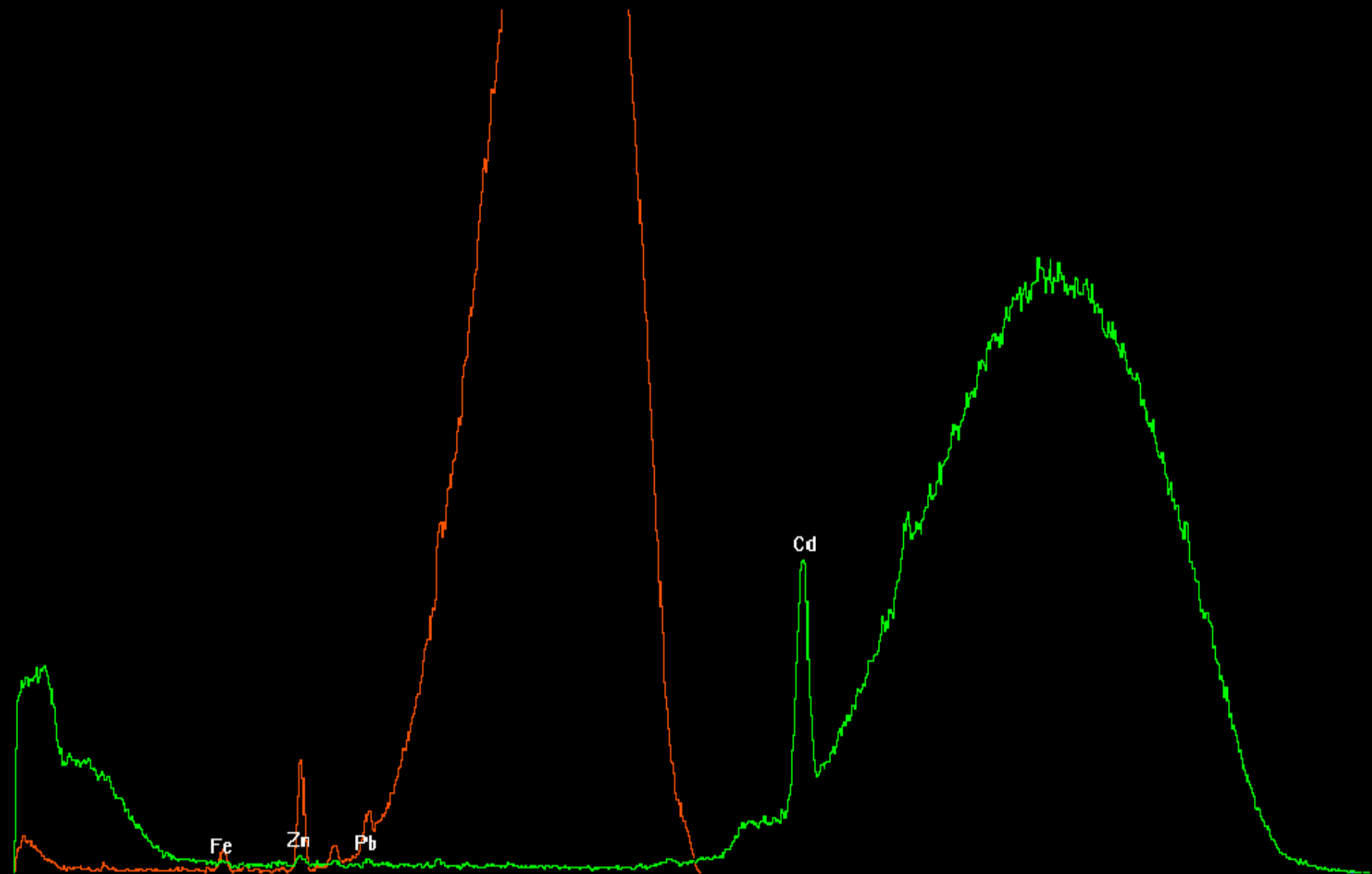
Liquid

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

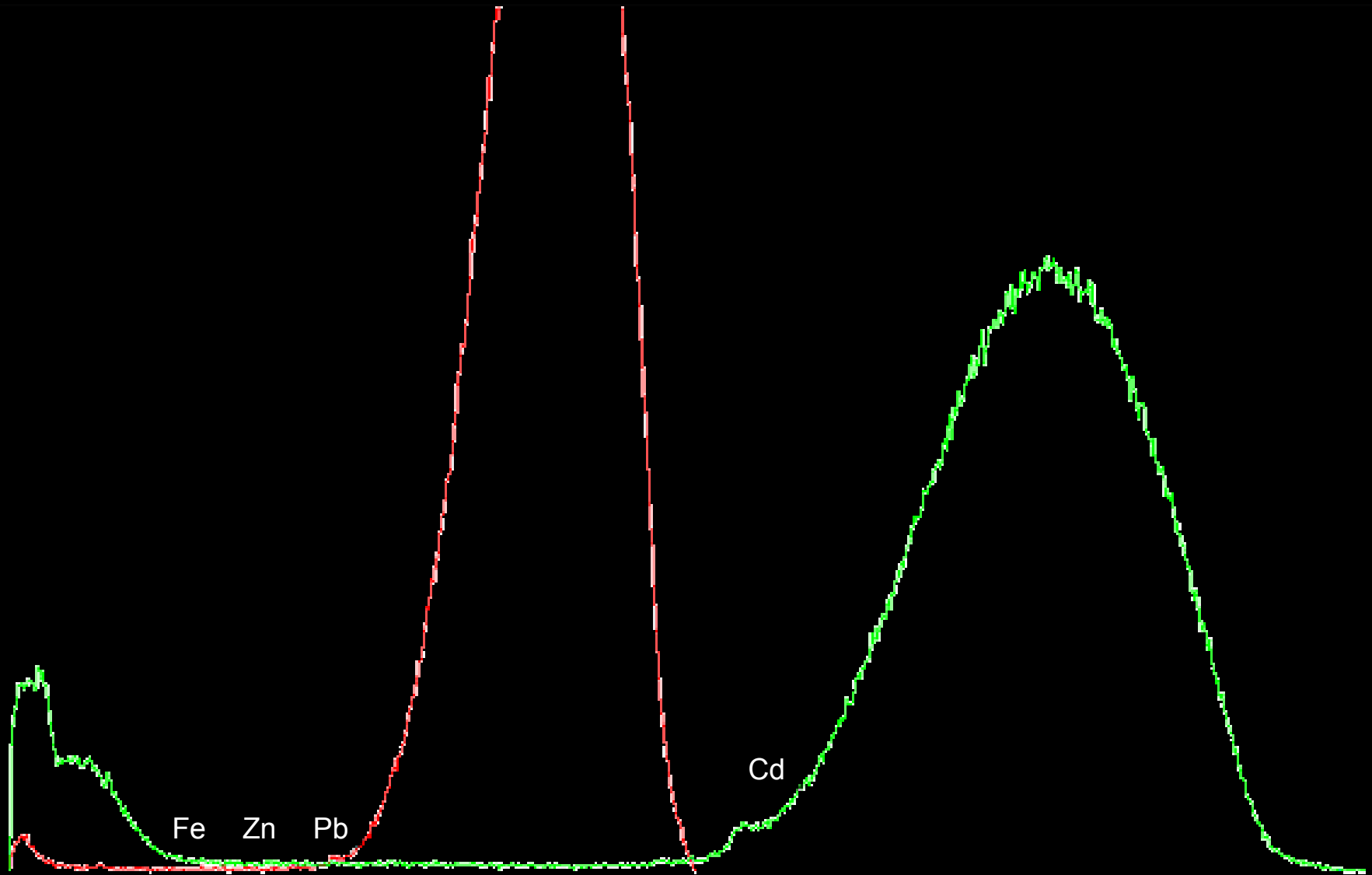
Liquid sample analysis results

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

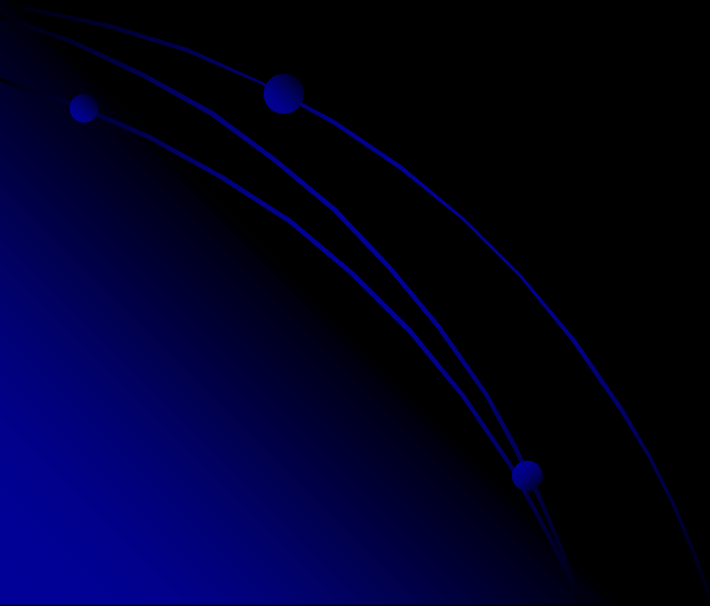


Resulting spectra with no compounds detected



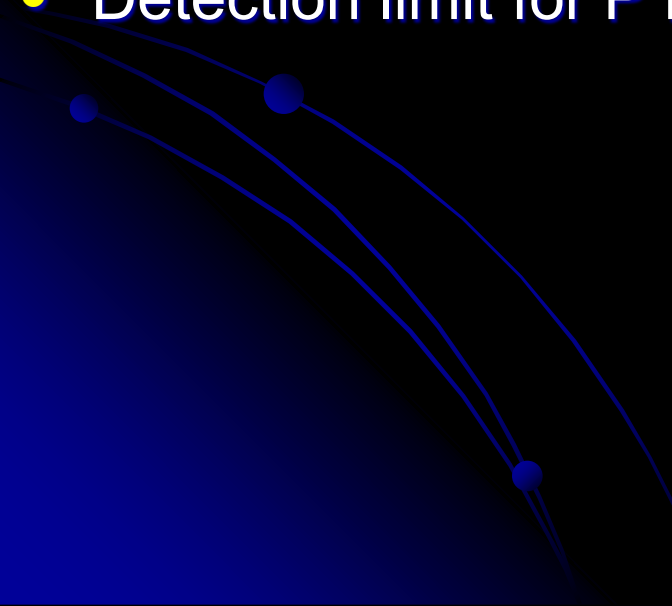
Conclusions

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



Analysis of Samples (III)

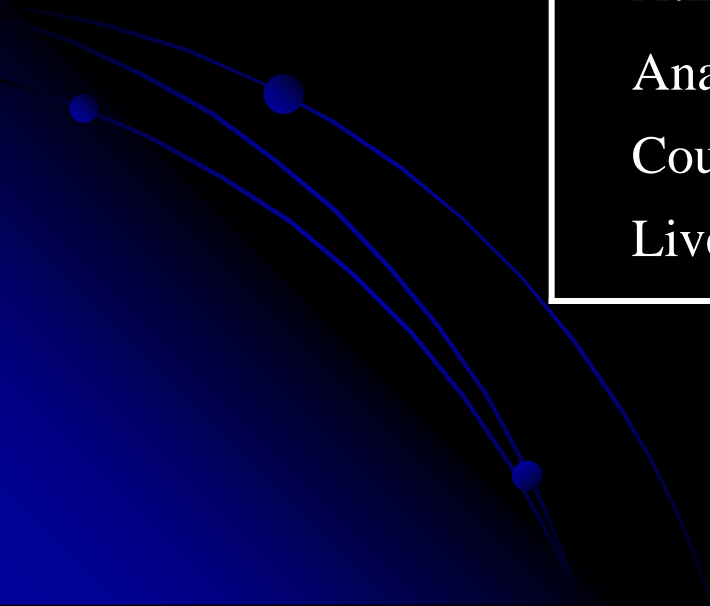
Oil

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

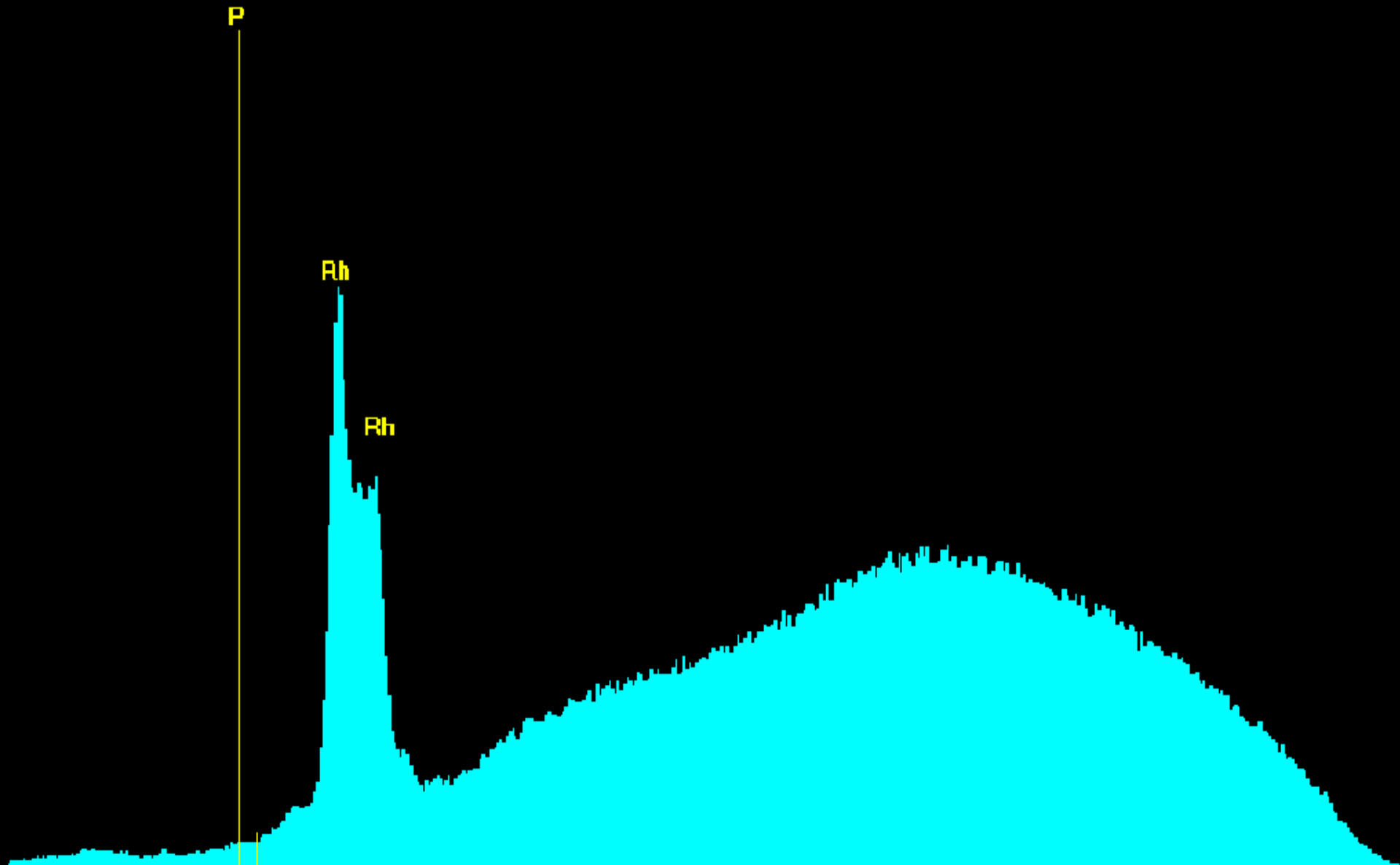
- Qualitative measurements of sunflower-oil and lecithin

Conditions used :

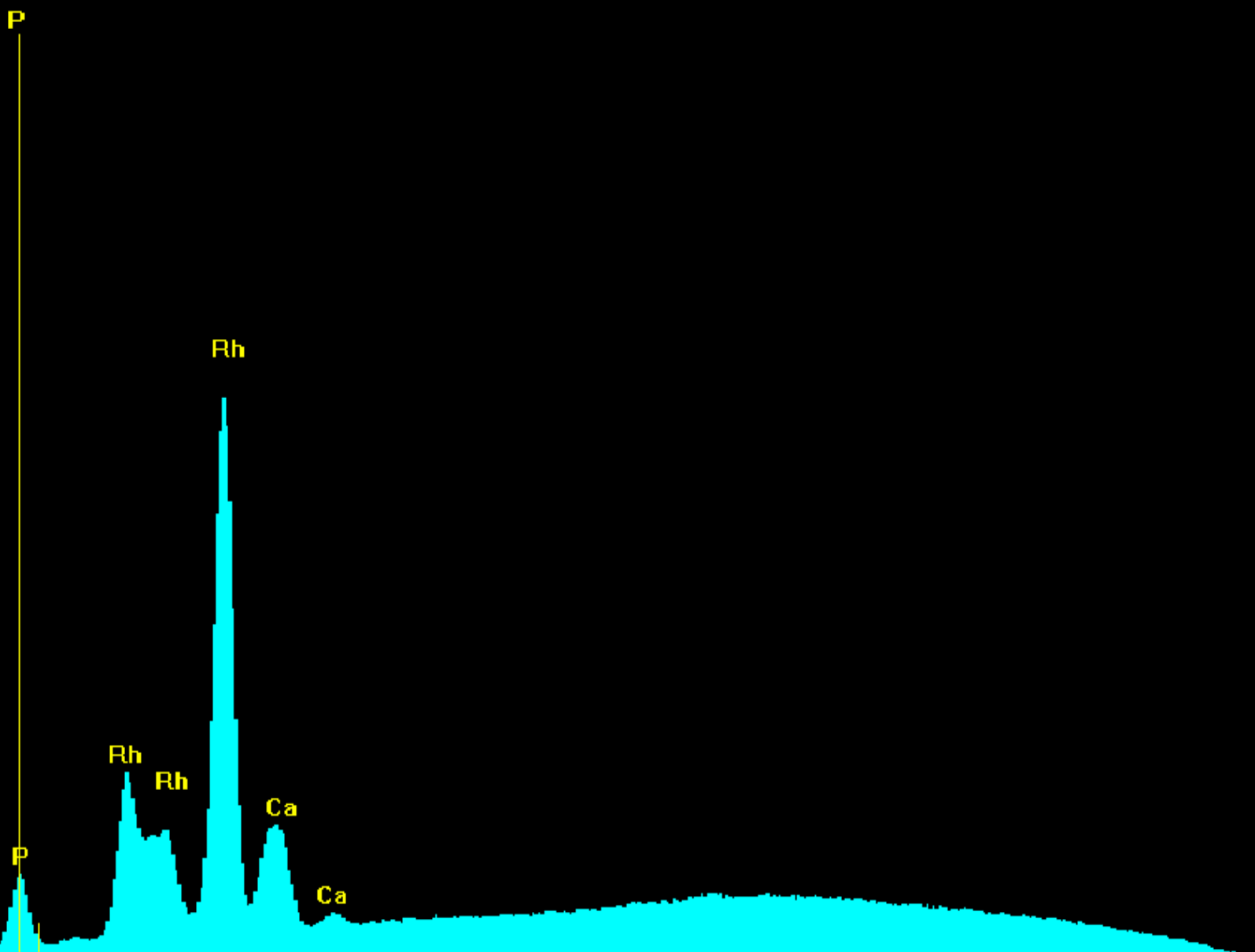
Condition name	Low Za
Filter	No filter
Voltage	4 kV
Atmosphere	Air
Analyzed element	P
Count Rate	Medium
Live Time	100 sec



Spectrum obtained performing qualitative analysis of sunflower oil



Spectrum obtained performing qualitative analysis of bolecht (lecithin)

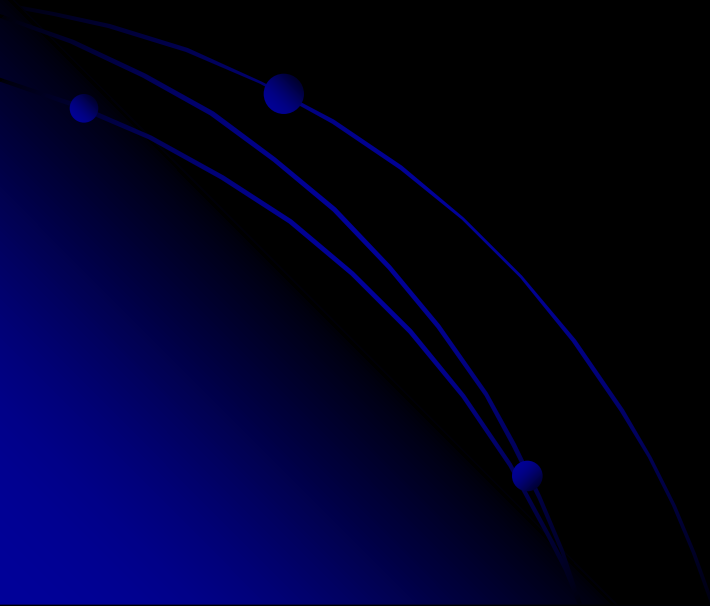


- Detection limit for P by adding bolect to sunflower oil

<u>MEASUREMENT</u>		<u>SPECTRA OBTAINED</u>
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 !

