

Sixth scientific seminar of INPOLDE interdisciplinary network

Project MIS ETC 1676

“Cross-border interdisciplinary cooperation for the prevention of natural disasters and mitigation of environmental pollution in Lower Danube Euroregion”



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Modern techniques used in environmental investigations

Trainer:

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The **most used** analytical techniques for elemental analysis (metals, metalloids, trace elements) in environmental studies are **spectrometric** techniques:

Atomic techniques

X-ray Fluorescence (XRF) (ED-XRF and WD-XRF)

Atomic Absorption Spectroscopy (AAS)

Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES)

Inductively Coupled Plasma–Mass Spectrometry (ICP-MS)

Nuclear techniques

Instrumental Neutron Activation Analysis (INAA)

Particle Induced X-ray Emission (PIXE)

Particle Induced Gamma-ray Emission (PIGE)



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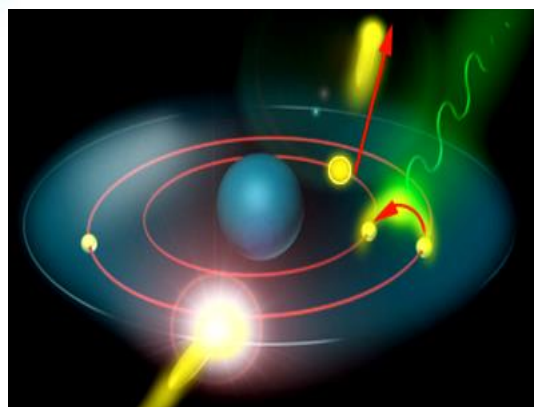
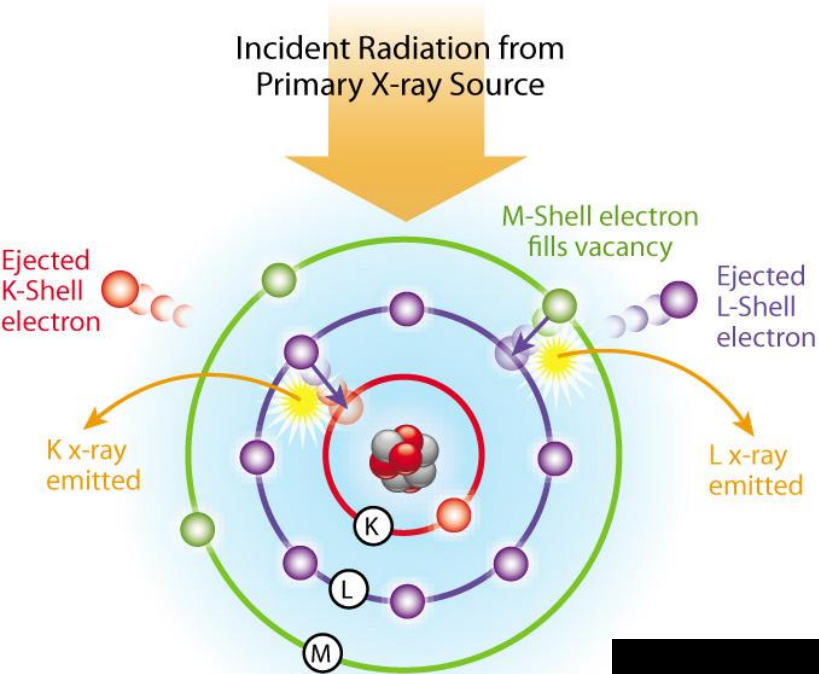
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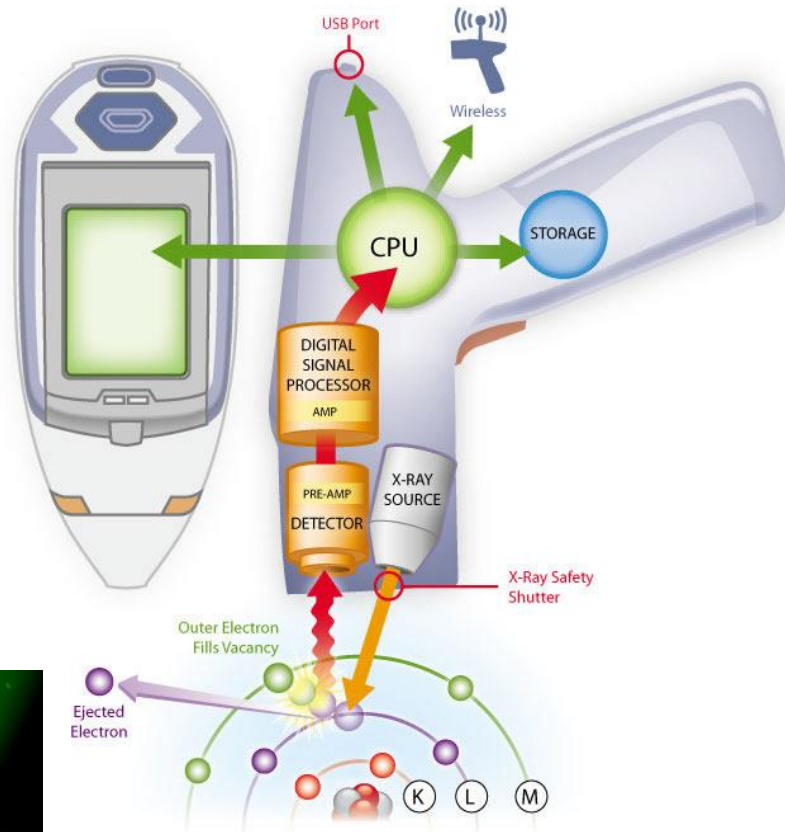
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XRF Excitation Model



Portable XRF Spectrometer



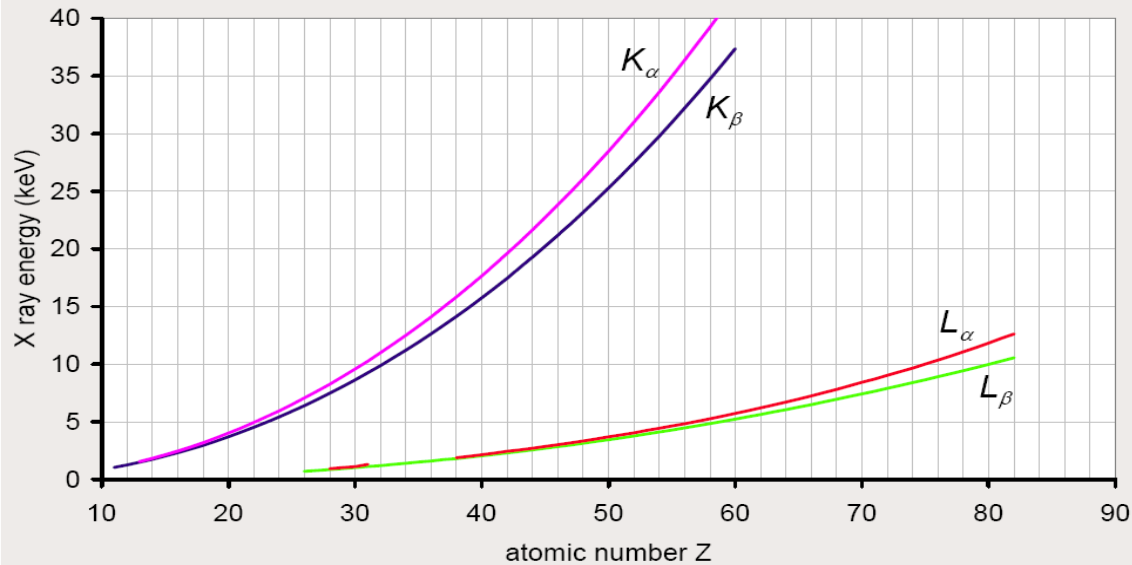
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The monotonic increase of the **X-ray energies** with the atomic number Z of the element (energies known and tabulated in the literature) as well as the proportionality of the **X-ray intensities** (peak areas) with the element concentration in the sample allow a **qualitative** and **quantitative** determination of the elemental contents in samples.

X-ray energies vs element



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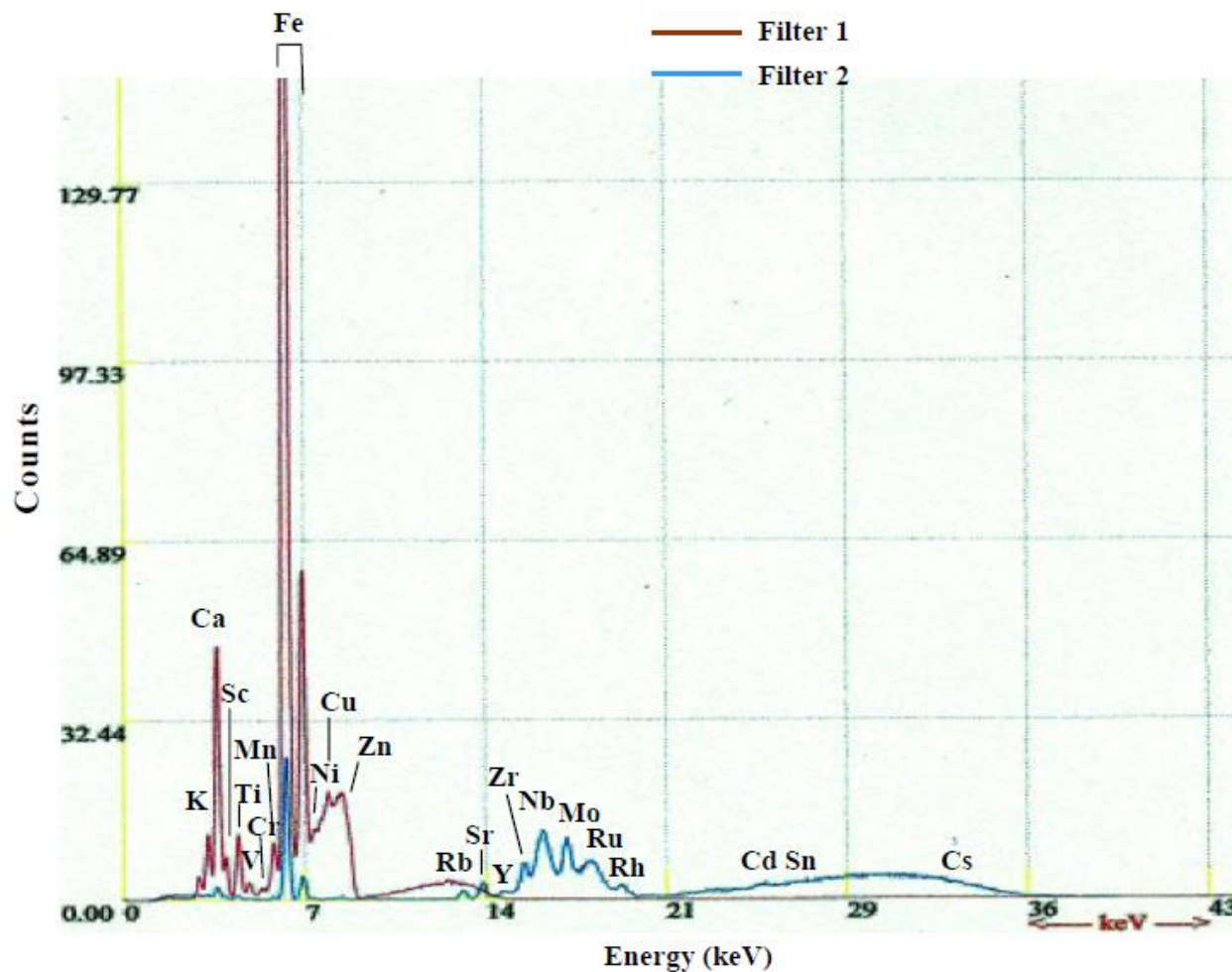
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XRF Spectrum of a soil sample

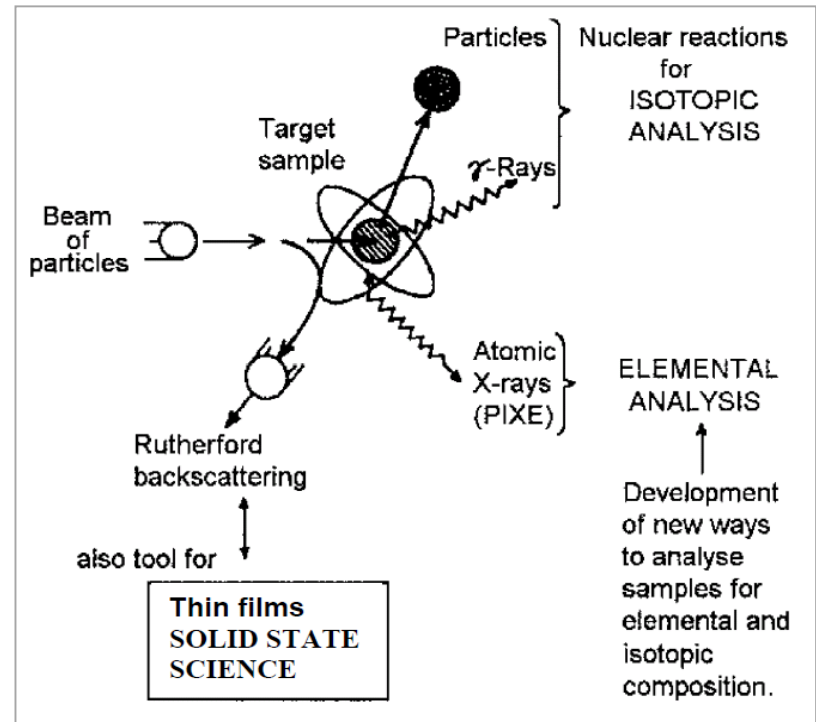
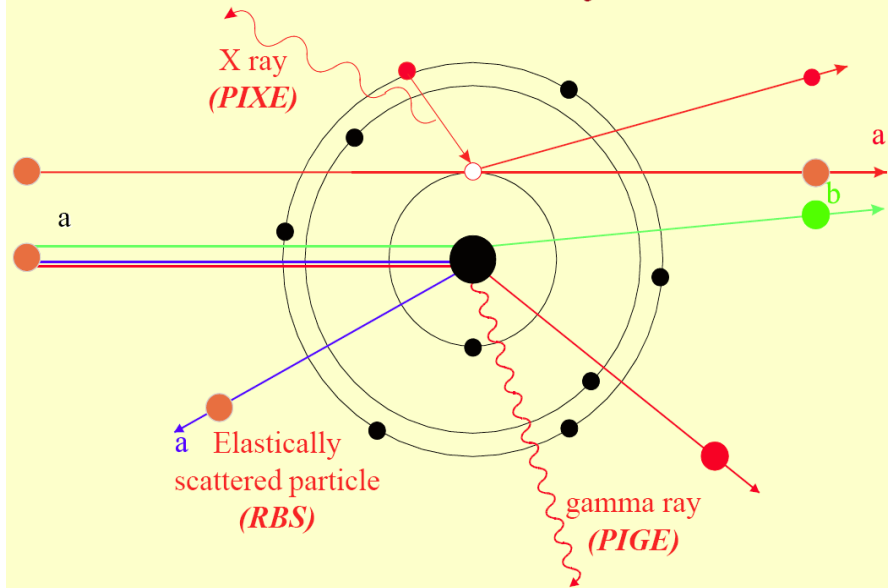


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Ion Beam Analysis



The **particle induced X-ray emission (PIXE)** technique is based on the ionization of atomic inner shells of a sample/target by a charged particle beam (**protons**, in particular) entering the target, followed by emission of the characteristic X-rays.

PIXE can be coupled with other ion beam analysis (IBA) techniques, such as **particle induced gamma-ray emission (PIGE)** or **Rutherford backscattering (RBS)**, and can be completed by **neutron activation analysis (NAA)**.

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Experiment proposal

Application of PIXE and PIGE techniques using a beam of **3 MeV protons** were carried out in order to determine elemental contents in

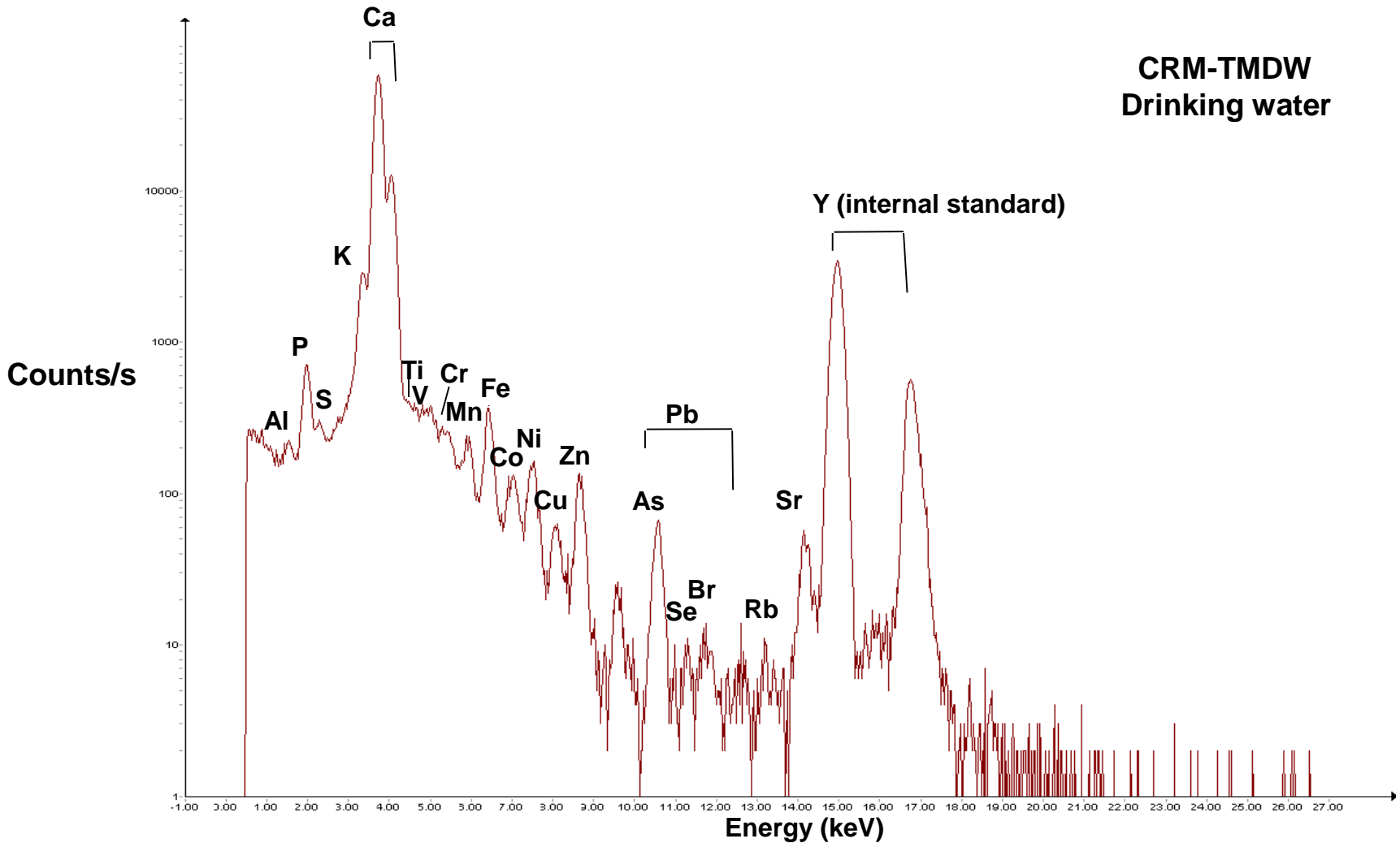
- **biological samples (tissues of molluscs, aquatic plants)**
and
- **environmental samples (sediments, soils)**

using comparator **standards of similar matrix**, prepared as **thick targets** (IAEA and NIST standards, as well as chemical compounds of elements to be determined).

The **elements of interest for PIXE** are: Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Br, Rb, Sr and Pb.

The **elements of interest for PIGE** are: F, Na, Mg, Al, Si, P, S, Cl, Cr, Mn, Fe, Cr, Co, and Cu.

**CRM-TMDW
Drinking water**



PIXE spectrum of a standard water sample using Si (Li) detector.



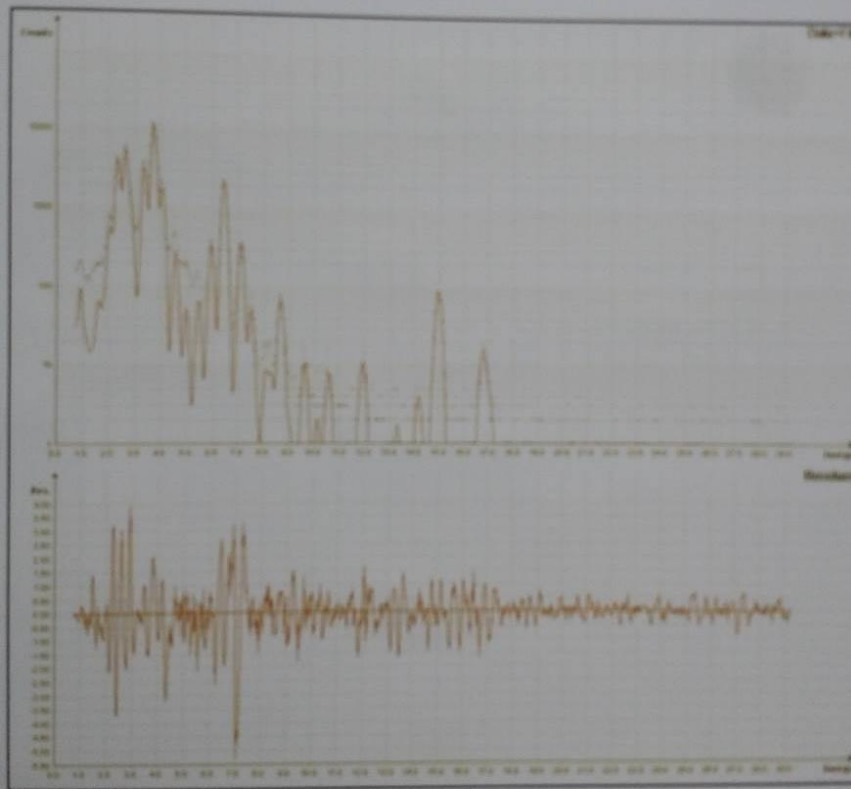
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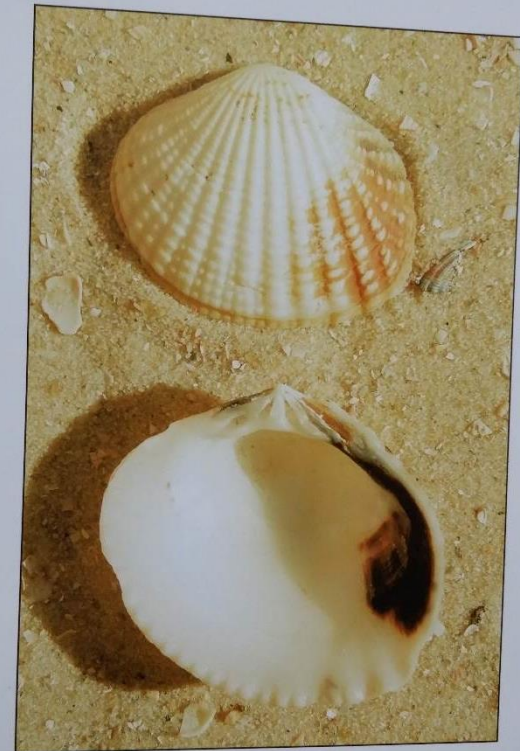
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*PIXE spectrum of Gafrarium tumidum sp.
and a GUPIX program fit.*



Gafrarium tumidum sp. (clams)

PIXE spectrum of a clam sample using Si (Li) detector.



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Sampling of environmental materials from Danube River



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Preparation of samples for nuclear analyses



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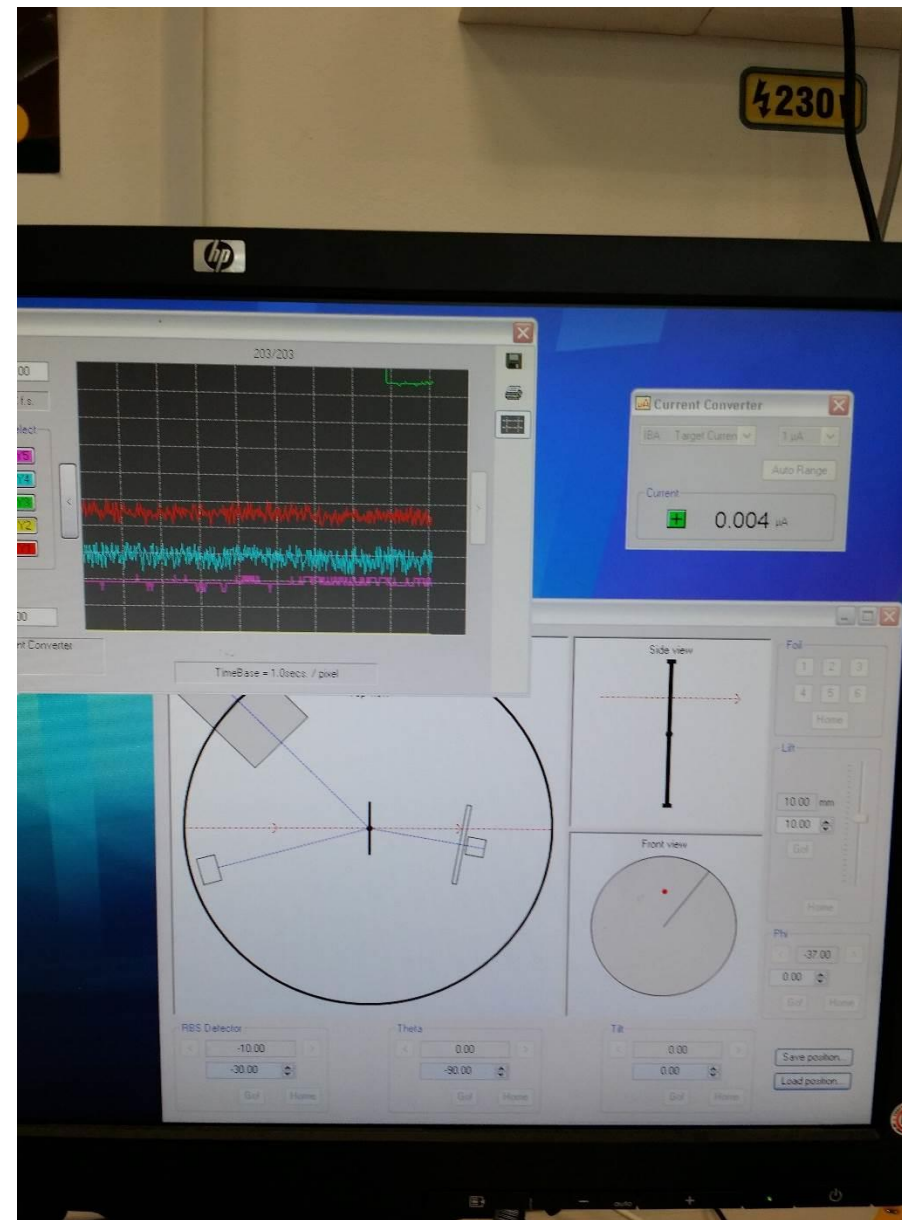
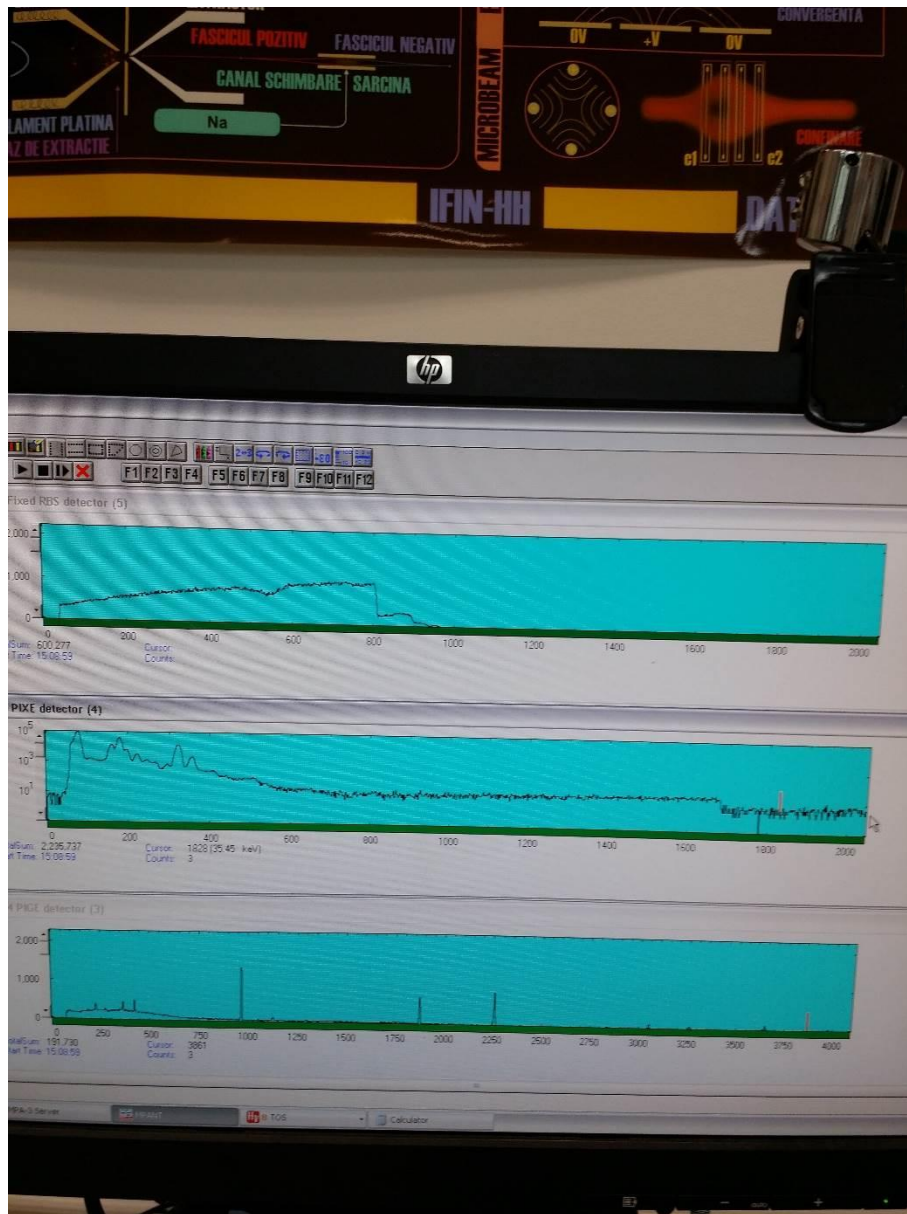
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PIXE-PIGE-RBS analysis system at nuclear tandem accelerator in Bucharest-Magurele



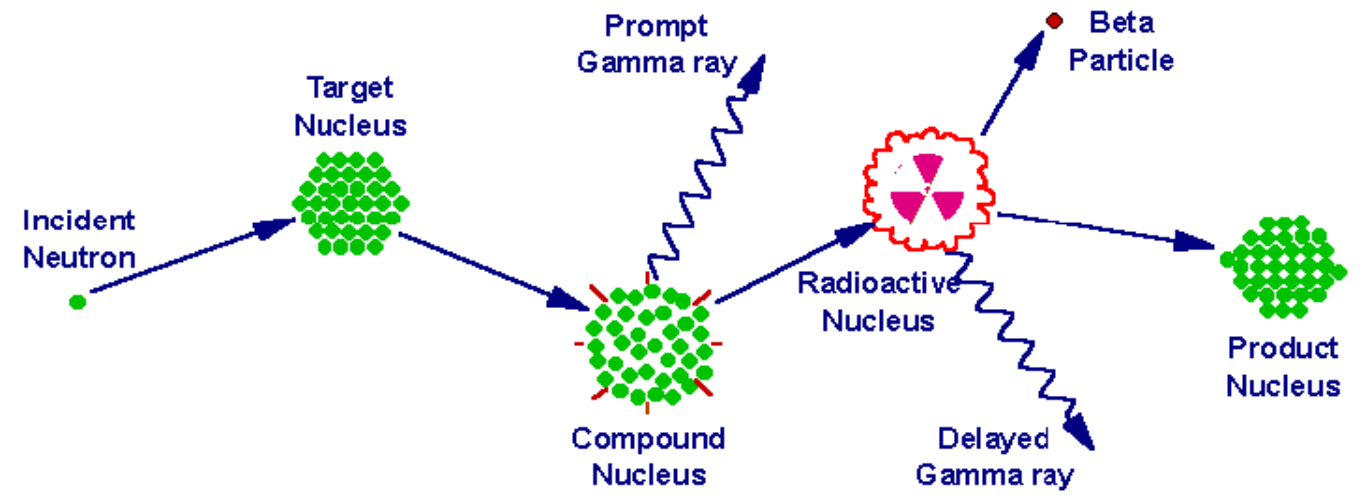
PIXE-PIGE-RBS spectra registered on-line simultaneously at nuclear tandem accelerator in Bucharest-Magurele

The PIXE and PIGE results will permit to:

- determine the regional extent of pollution with heavy metals and toxic elements and
- to identify the specially affected areas and local sources of pollution.

This collaboration will enforce the research partnership of Romanian institutions (UDJG, IFIN-HH) with research institutes from other countries and will have in view the enlargement of the research network.

Sequence of events occurring during the most common type of nuclear reaction used for INAA - (n,gamma) reaction



When a neutron interacts with the target nucleus via a non-elastic collision, a compound nucleus forms in an excited state. The excitation energy of the compound nucleus is due to the binding energy of the neutron with the nucleus. The compound nucleus will almost instantaneously de-excite into a more stable configuration through emission of one or more characteristic prompt gamma rays. In many cases, this new configuration yields a radioactive nucleus which also de-excites (or decays) by emission of one or more characteristic delayed gamma rays. Depending upon the particular radioactive species, half-lives can range from fractions of a second to several years.

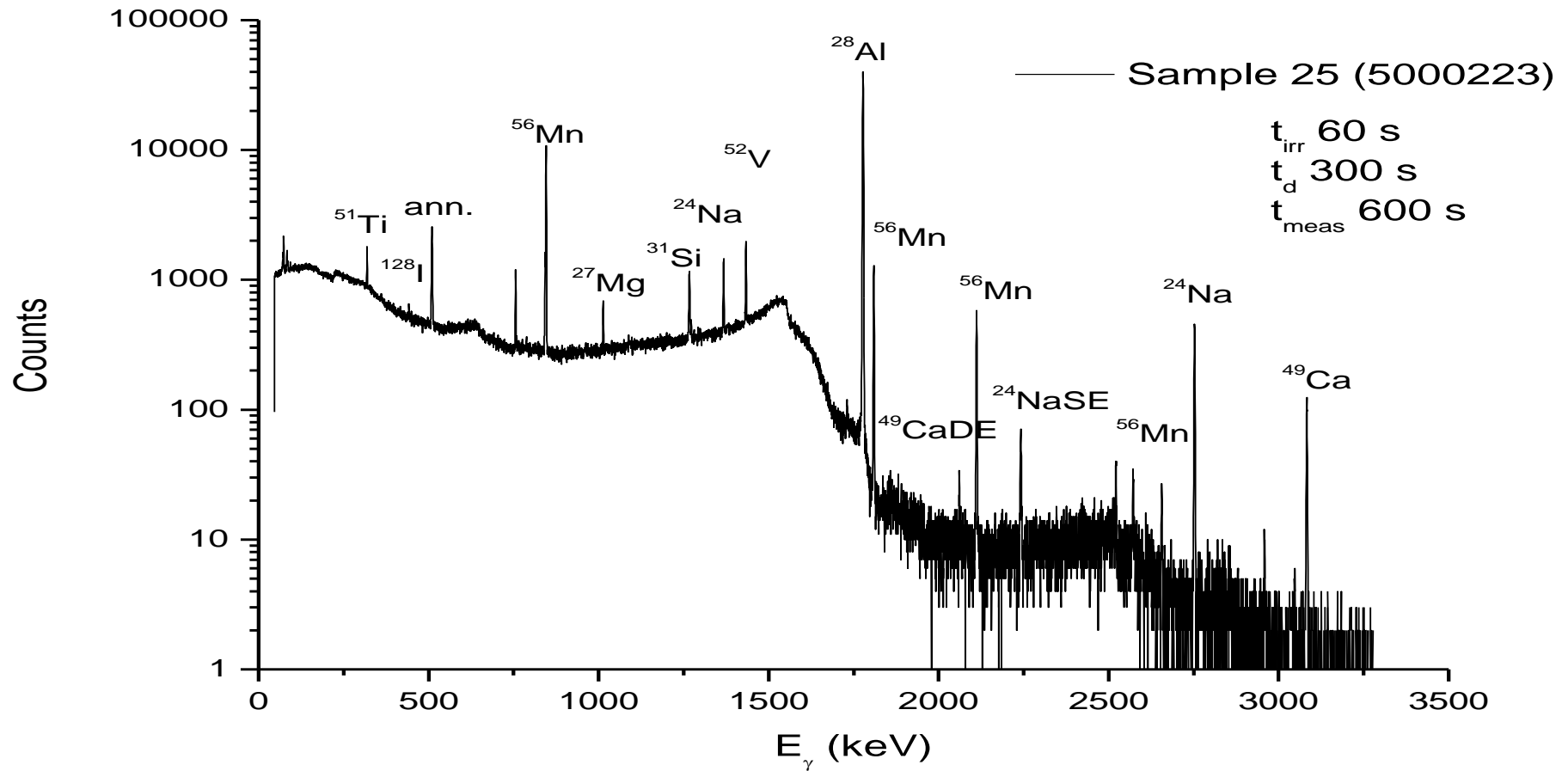


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Short irradiation INAA spectrum of a soil sample collected from an iron and steel industrialized region at Galati (RO)

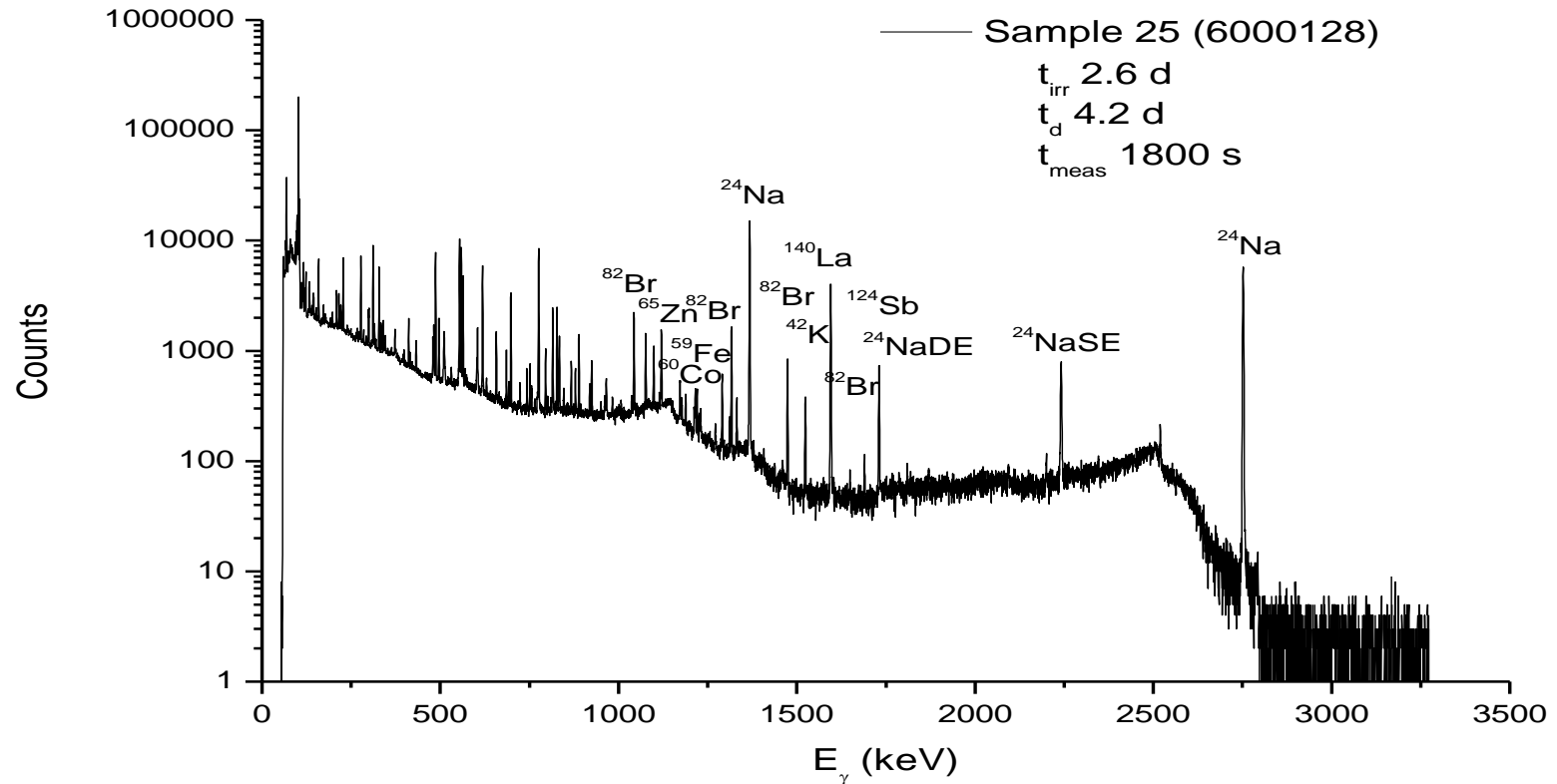


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Long irradiation INAA spectrum of a soil sample collected from an iron and steel industrialized region at Galati (RO)



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Atomic Absorption Spectroscopy (AAS) – principle

ATOMIC ABSORPTION SPECTROSCOPY (AAS) is an analytical technique that measures the concentrations of elements in different samples, making use of the absorption of light by these elements.

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Atomic Absorption Spectroscopy (AAS) – principle

In AAS, light of a specific wavelength is passed through the atomic vapor of an element of interest, and measurement is made of the attenuation of the intensity of the light as a result of absorption.

Samples to be analyzed by AA must be **vaporized** or **atomized**, typically by using a **flame** or **graphite furnace**.

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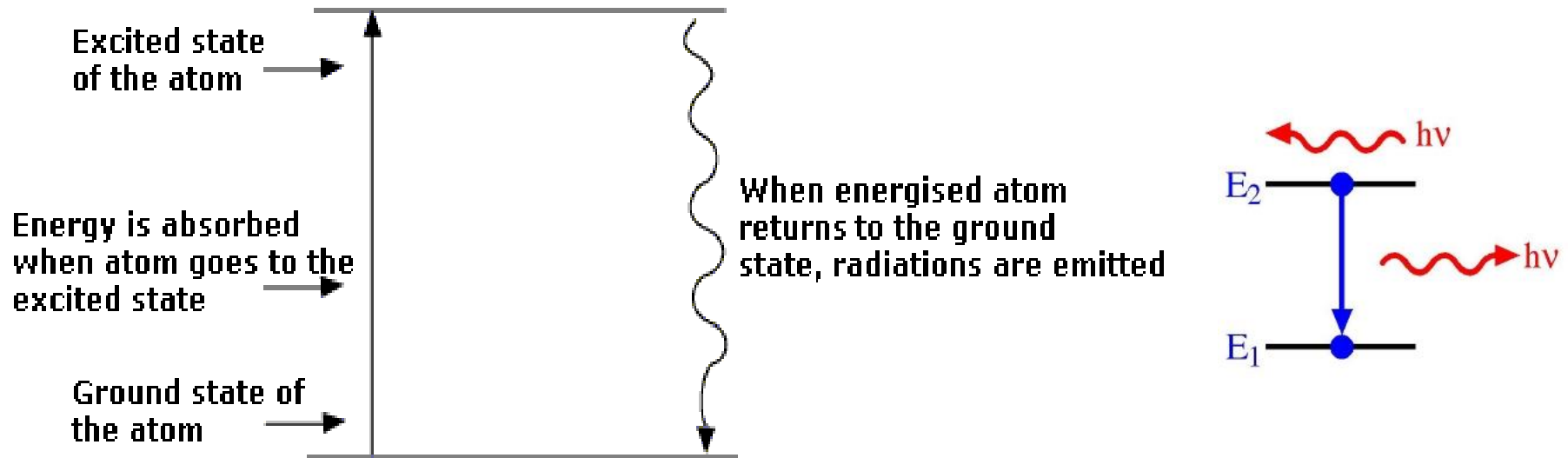
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- Atomic-absorption spectroscopy quantifies the absorption of **ground state atoms** in the **gaseous state** .
- The metal atoms absorb ultraviolet or visible light and make transitions to higher electronic energy levels. The analyte's concentration is determined from the amount of absorption.



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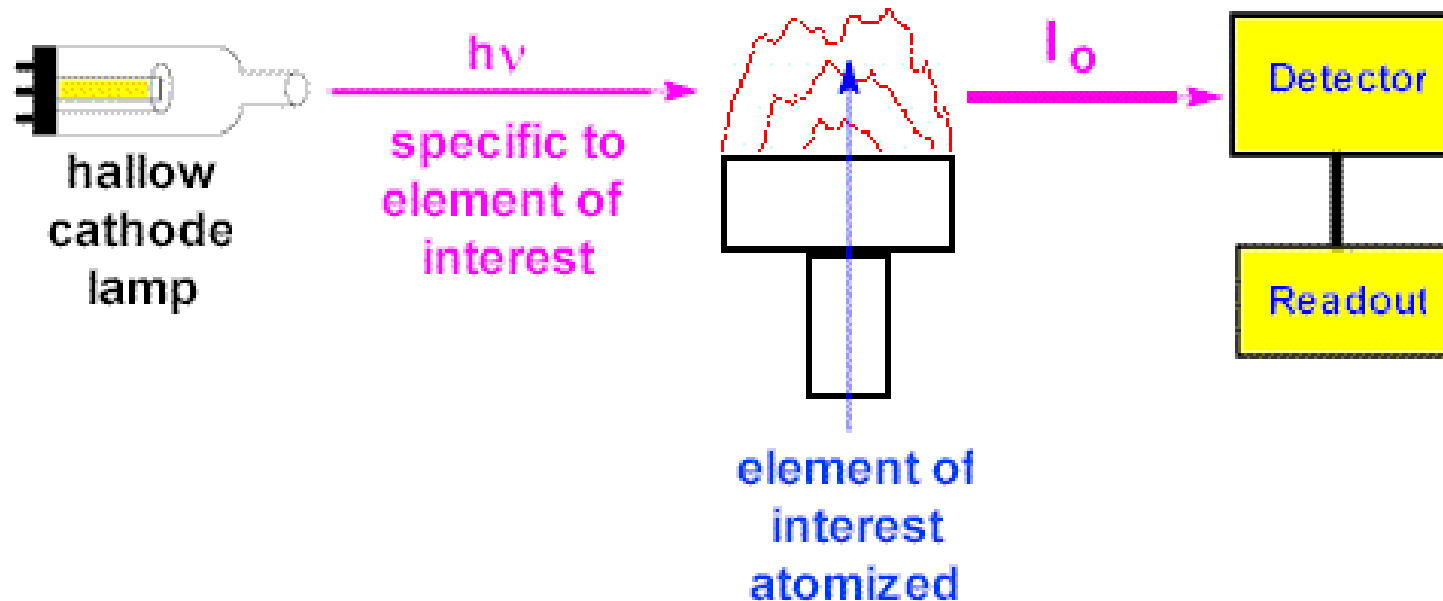
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Atomic Absorption Spectroscopy (AAS) – principle



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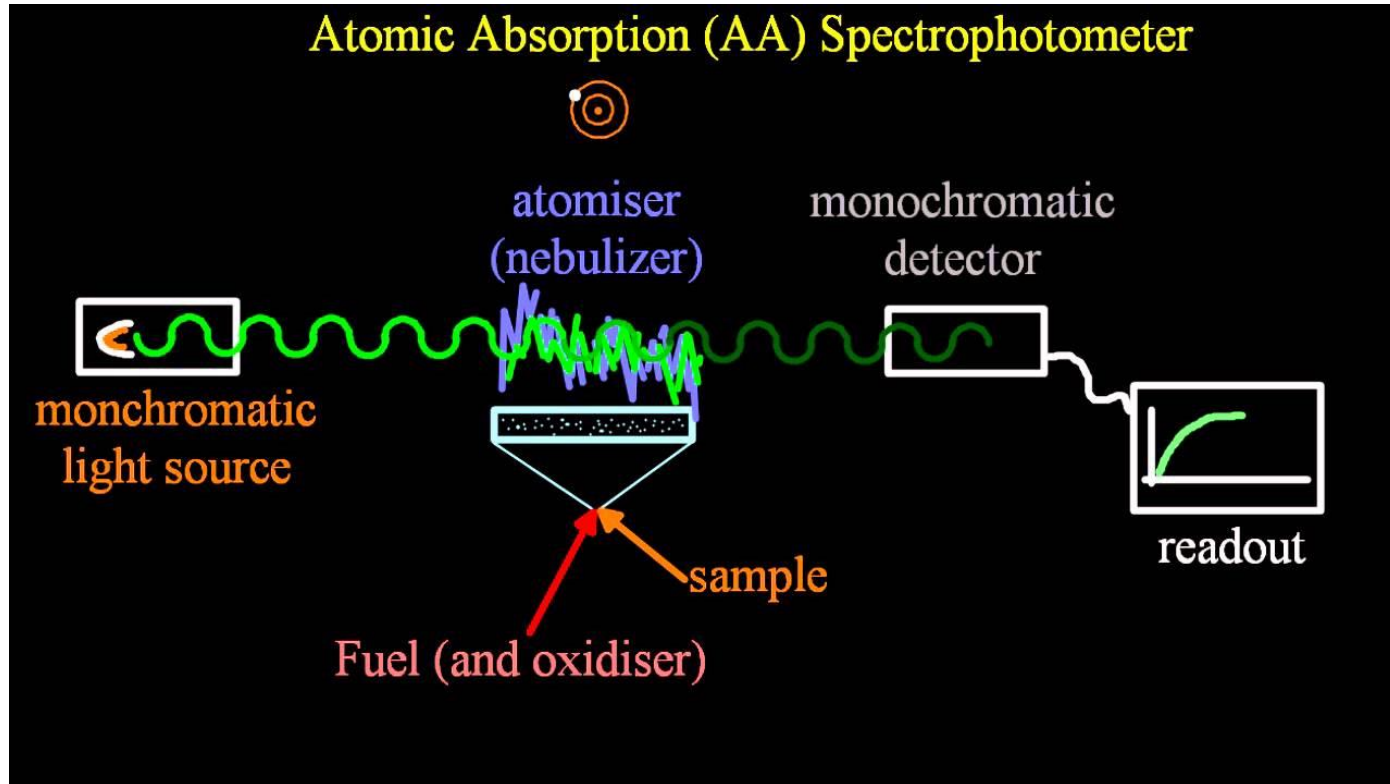


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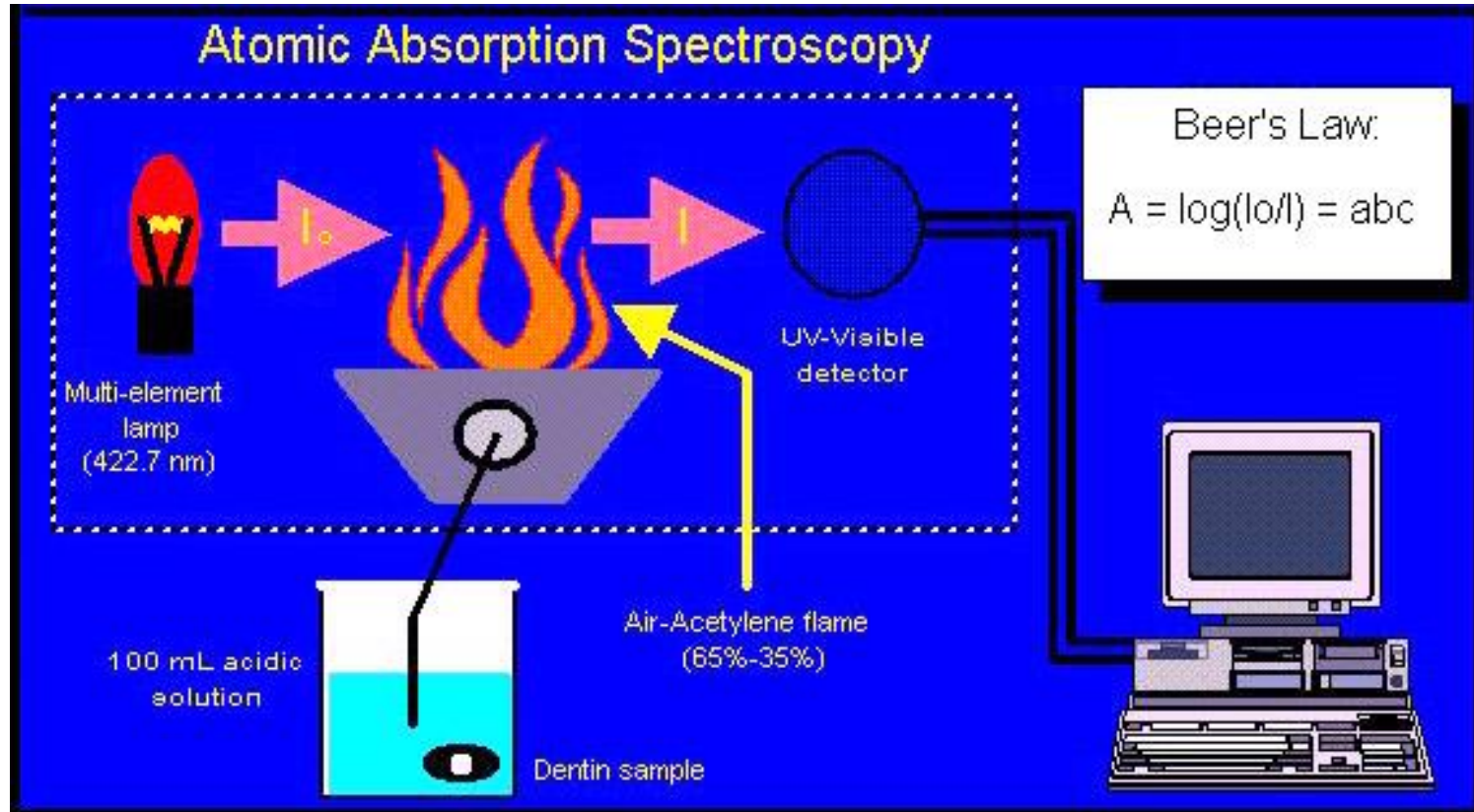
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Schematic diagram of a flame AAS spectrophotometer



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The **graphite furnace** is an electrothermal atomizer system that can produce temperatures as high as 3,000°C. The heated graphite furnace provides the thermal energy to break chemical bonds within the sample and produce free ground-state atoms. Ground-state atoms then are capable of absorbing energy, in the form of light, and are elevated to an excited state. The amount of light energy absorbed increases as the concentration of the selected element increases.

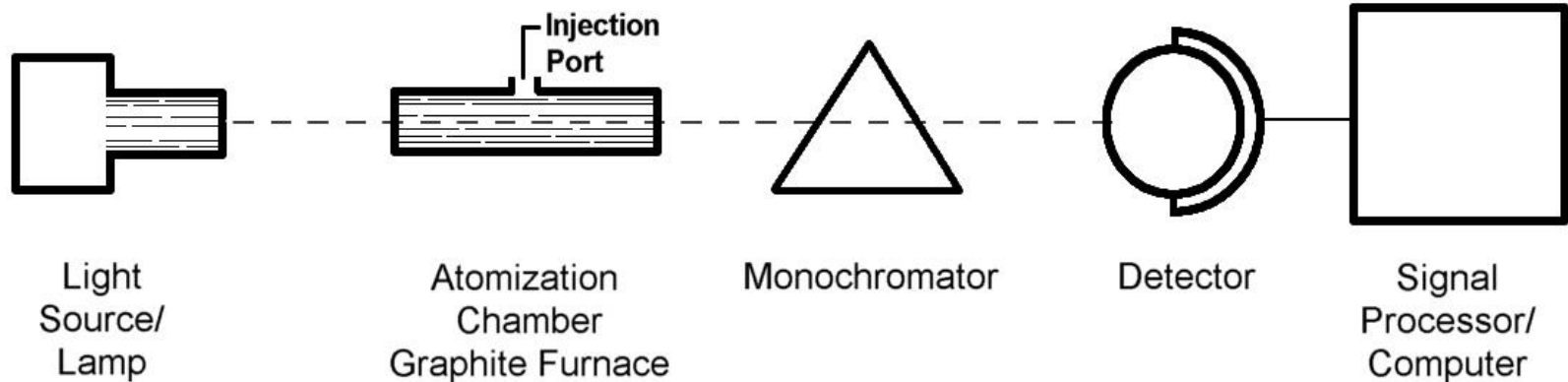


Diagram of the basic components of a Graphite Furnace Atomic Absorption Spectrometer.

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Atomic Absorption Spectroscopy (AAS) – principle

- Concentration measurements** are usually determined from a working curve after calibrating the instrument with standards of known concentration.
- Quantitative analysis by AA depends on:
 - (1) accurate measurement of the intensity of the light and
 - (2) the assumption that the radiation absorbed is proportional to atomic concentration.

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High-Resolution Continuum Source AAS (**HR-CS AAS**)

Thanks to a Xenon lamp as radiation source every wavelength of every element is available for analysis. Any number of elements can be combined in an analytical method.

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Detection Limits

HR-CS AAS

Symbol	Wave-length	HR-CS AAS		
		Flame mg/l	Graphite* µg/l	Hydride/CV µg/l
Ag	328.1	0.001	0.02	
Al	309.3	0.022*	0.01	
As	193.7	0.15	0.2	0.05/0.01
Au	242.8	0.005	0.03	
B	249.8	0.22	20	
Ba	553.6	0.01	0.3	
Be	234.9	0.001	0.01	
Bi	223.1	0.02	0.1	
Ca	422.7	0.002	0.005	
Cd	228.8	0.0004	0.002	
Co	240.7	0	0.02	
Cr	357.9	0.005	0.01	
Cs	852.1	0.02	0.05	
Cu	324.8	0.001	0.02	
Dy	404.6	0.11	0.4	
Er	400.8	0.06	3	
Eu	459.4	0.04	0.1	
Fe	248.3	0.001	0.01	
Ga	287.4	0.15	0.08	

Detection Limits

HR-CS AAS

Symbol	Wave-length	HR-CS AAS		
		Flame mg/l	Graphite* µg/l	Hydride/CV µg/l
Gd	407.9	9	200	
Ge	265.2	0.25	0.3	
Hf	286.6	2.5	-	
Hg	253.7	-	-	0.1/0.01
Ho	405.4	0.04	8	
In	325.6	0.04	0.5	
Ir	208.9	2	1.5	
K	766.5	0.003	0.001	
La	550.1	4	300	
Li	670.8	0.0007	0.03	
Lu	336.0	1	100	
Mg	285.2	0.0001	0.001	
Mn	279.5	0.001	0.006	
Mo	313.3	0.015	0.08	
Na	589.0	0.002	0.001	
Nb	334.4	5	-	
Nd	463.4	2	-	
Ni	232.0	0.0012	0.04	
Os	290.9	-	-	



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Detection Limits

HR-CS AAS

Symbol	Wave-length	HR-CS AAS		
		Flame mg/l	Graphite* μg/l	Hydride/CV μg/l
P	213.6	100	100	
Pb	217.0	0.005	0.03*	
Pd	247.6	0.01	0.04	
Pr	495.1	4	200	
Pt	265.9	0.1	0.6	
Rb	780.0	0.002	0.03	
Re	346.0	0.5	-	
Rh	343.5	0.03	0.09	
Ru	349.9	0.05	0.7	
Sb	217.6	0.12	0.2	0.3/0.04
Sc	391.2	0.2	-	
Se	196.0	0.06	0.3	0.2/0.02
Si	251.6	0.08	0.1	
Sm	429.7	0.8	30	
Sn	224.6	0.08	0.2	0.5/0.03
Sr	460.7	0.001	0.2	

Detection Limits

HR-CS AAS

Symbol	Wave-length	HR-CS AAS		
		Flame mg/l	Graphite* μg/l	Hydride/CV μg/l
Ta	271.5	1.6.	-	
Tb	432.6	1.2.	-	
Te	214.3	0.08	0.2	
Ti	365.4	0.1	0.5	
Tl	276.8	0.02	0.2	
Tm	371.8	-	0.2	
U	358.5	-	-	
V	318.4	0.06	0.1	
W	255.1	1	-	
Y	410.2	0.3	-	
Yb	398.8	0.007	0.05	
Zn	213.9	0.001	0.003	
Zr	360.1	-	-	

* Graphite Mode using peak height
 * Measured with ultra pure chemicals under clean room conditions
 * Sample volume 20μL

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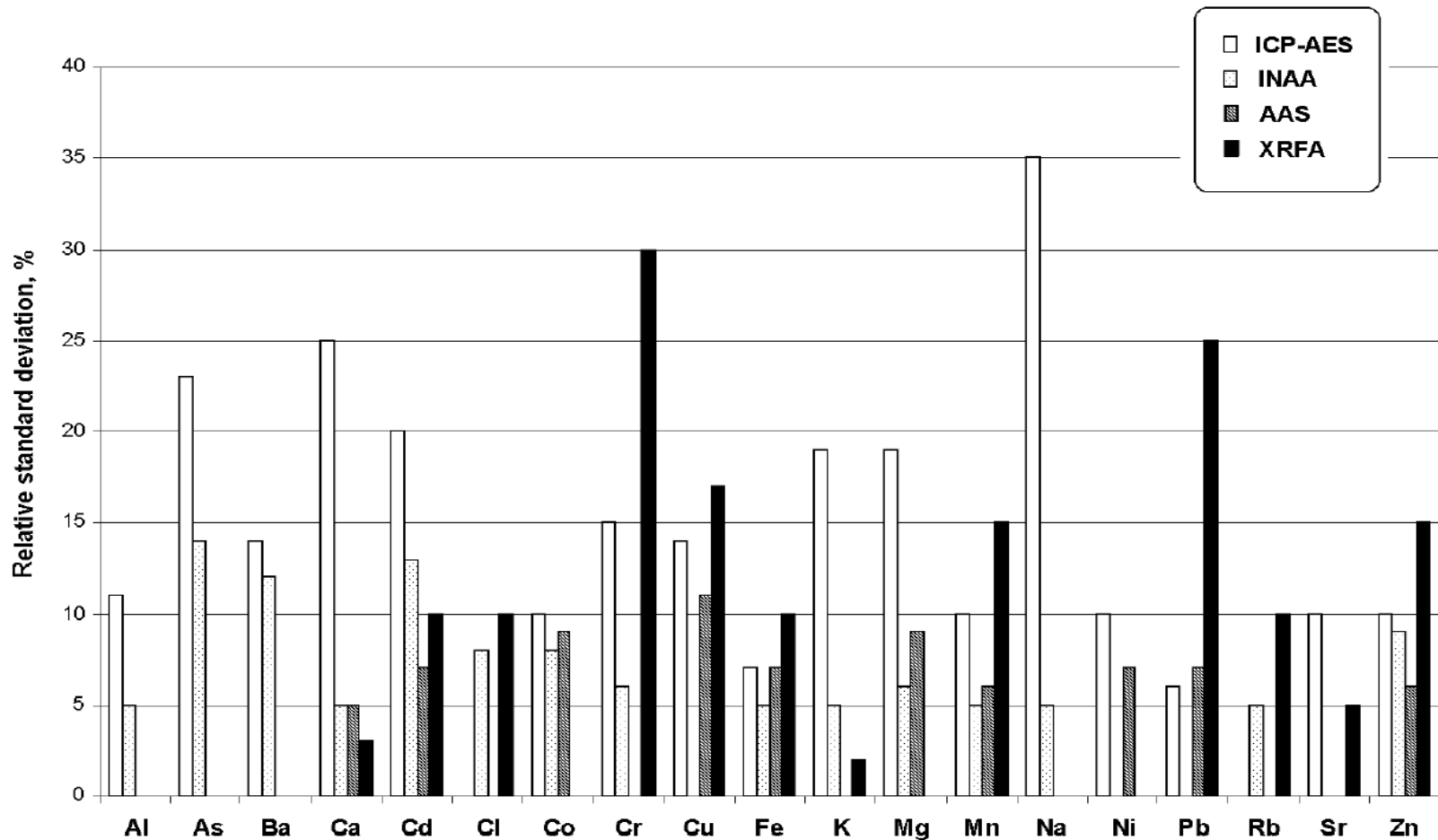
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Comparison of the precision of ICP-AES, INAA, AAS and ED-XRF at the determination of essential and toxic elements in plant samples

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Element	INAA	ED-XRF	PIXE	ICP-AES	ETA-AAS	ICP-MS
V	0.03	20	1.3	3.5	0.2	0.03
Cr	0.03	16	0.8	4	0.01	0.06
Mn	0.001	12	0.6	0.95	0.01	0.10
Fe	6	12	0.5	3	0.02	
Ni	3	5	0.4	6.5	0.2	0.10
Cu	0.03	6	0.3	3.5	0.02	0.32
Zn	0.3	5	0.3	1.2	0.001	0.21
As	0.03	4	0.4	35	0.2	0.04
Se	0.03	2	0.4	50	0.5	0.79
Mo	0.3	5	1.9	5.5	0.02	0.04
Cd	0.6	6	10	1.7	0.003	0.06
In	0.0006		14	40		0.07
Sn	1	8	16	17	0.1	0.06
Sb	0.01	8	14	20	0.1	0.05
Hg	0.003	7	1.0	17	2	0.02
Tl			1.1	25	0.1	
Pb		8	1.1	30	0.05	0.05

Detection limits, in mg/kg solid sample, for 17 elements in six analytical techniques

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