

Instrumental Neutron Activation Analysis (INAA) and X-ray Fluorescence (XRF) Analysis – Practice and Applications



Instrumental Neutron Activation Analysis Laboratory – University of Massachusetts, Lowell, USA

Philips PW2400 Sequential Wavelength Dispersive X-ray Fluorescence Spectrometer — Department of Geological Sciences, University of Canterbury, NZ

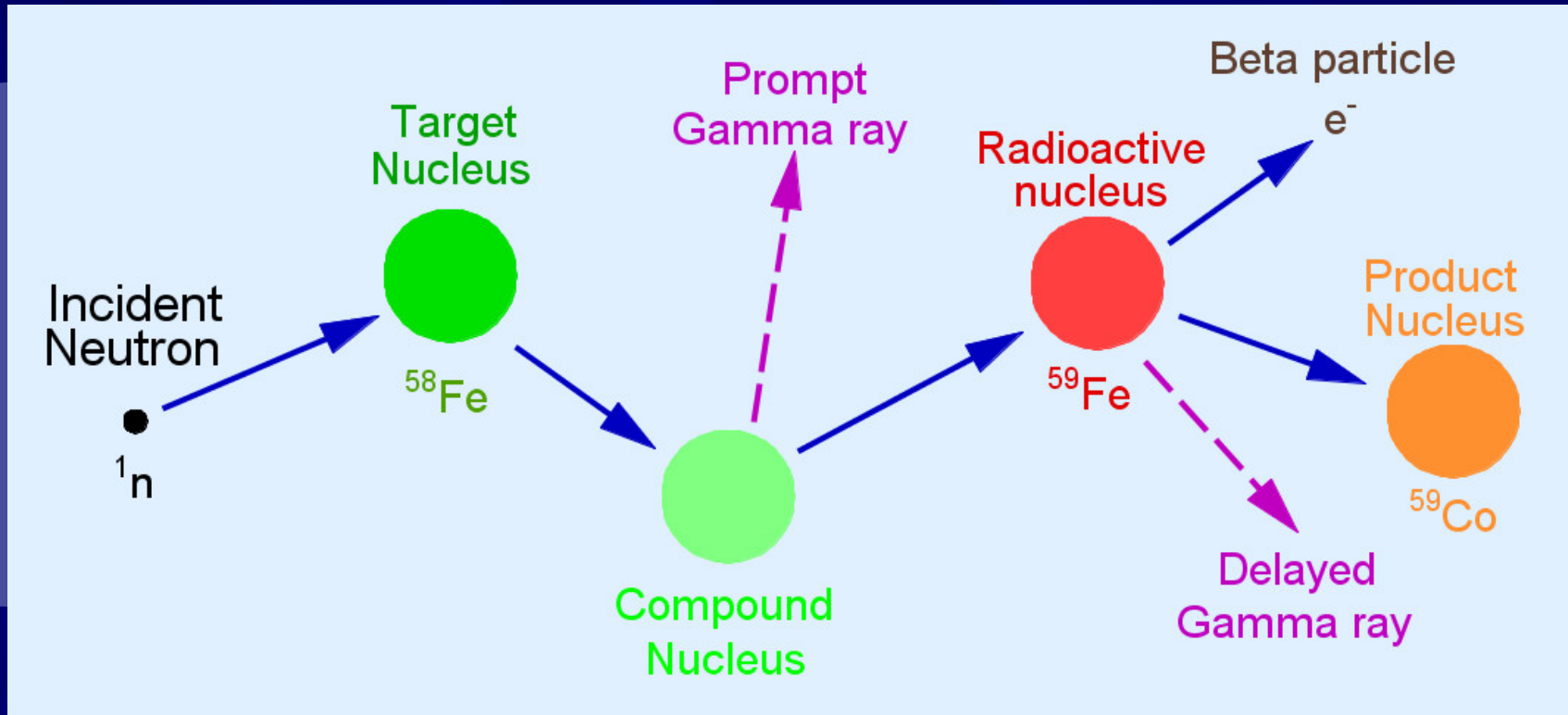


Principles of Instrumental Neutron Activation Analysis (INAA)



The n-gamma Reaction

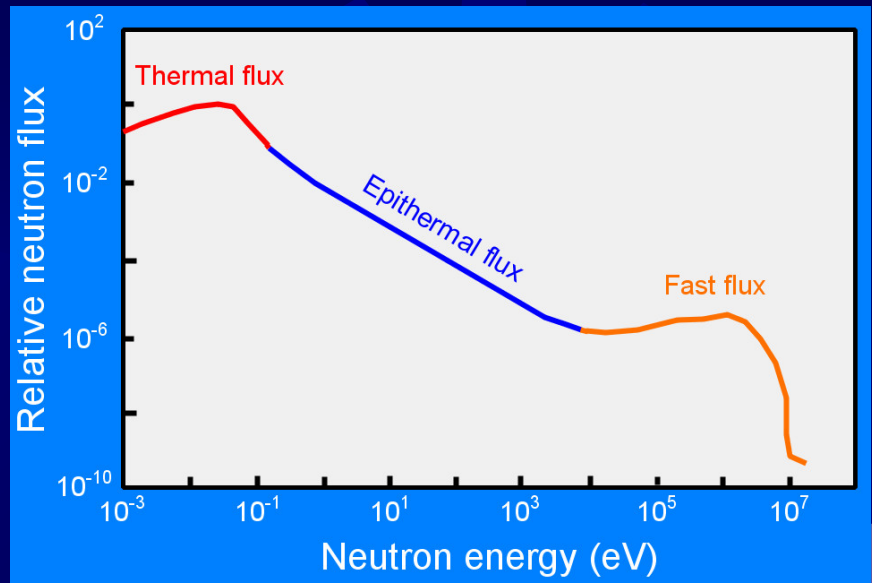
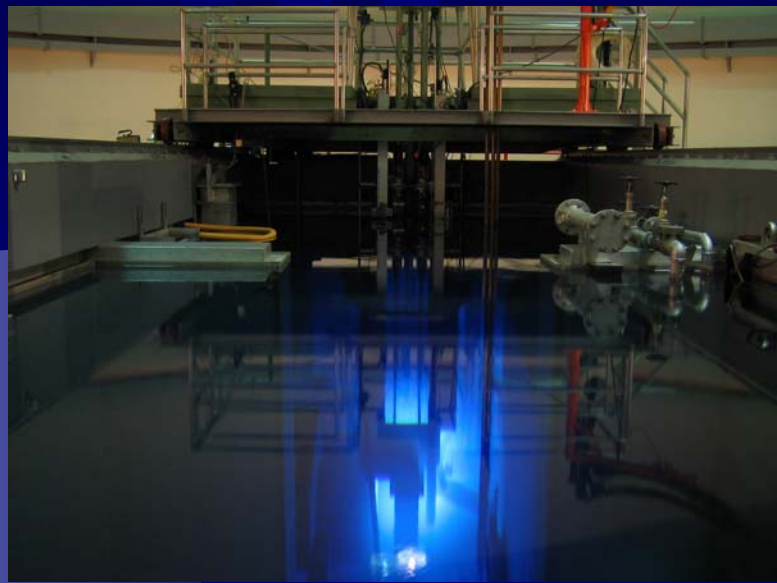
The basic reaction for INAA



Example: ${}^{58}\text{Fe} + {}^1_0\text{n} \longrightarrow {}^{59}\text{Fe} + \text{Beta}^- + \text{gamma rays}$

Gamma ray energies = 142.4, 1099.2, 1291.6 KeV

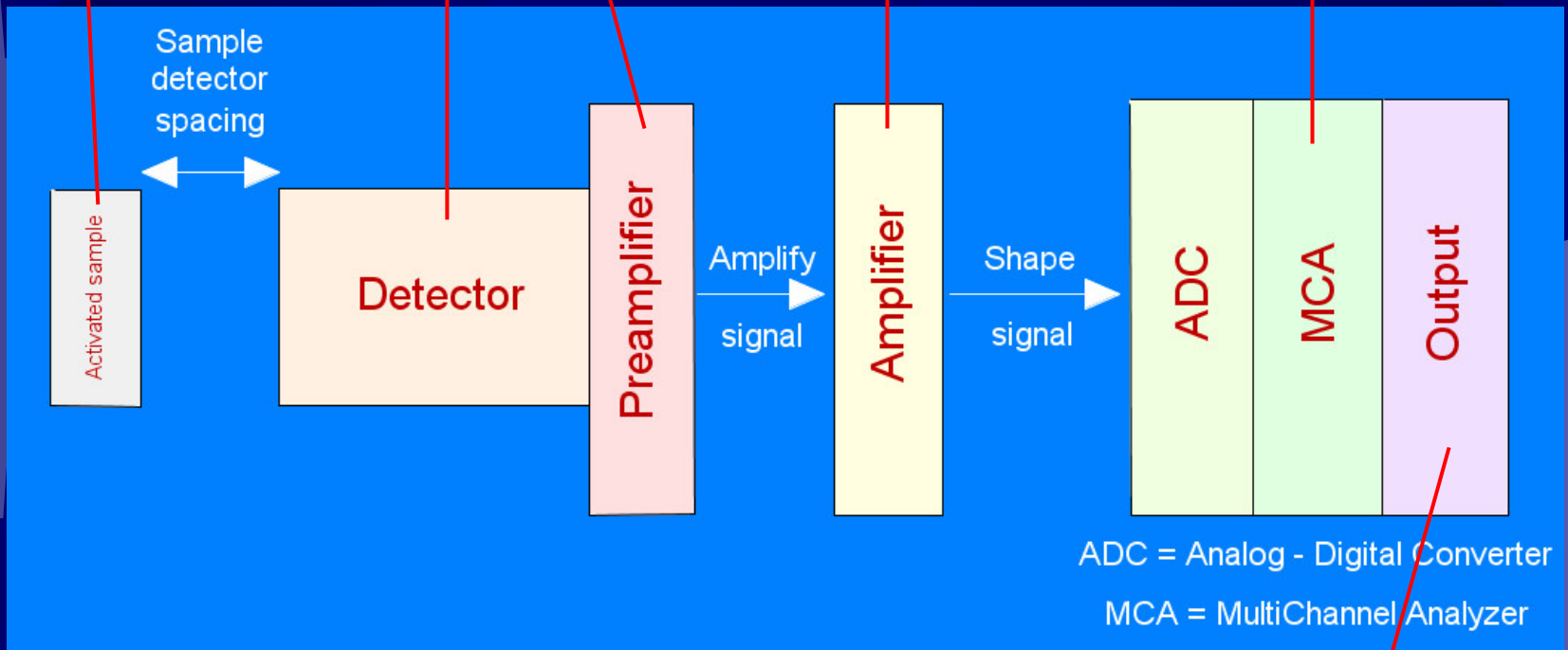
Different neutron energies are used for different types of experiments.



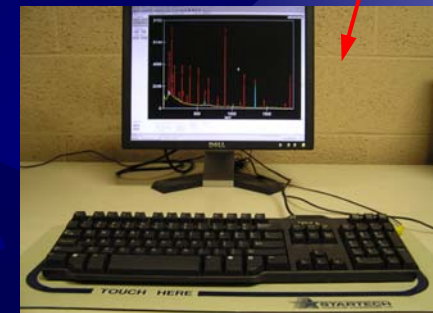
UML 1 Mw Research Reactor

The Neutron Source



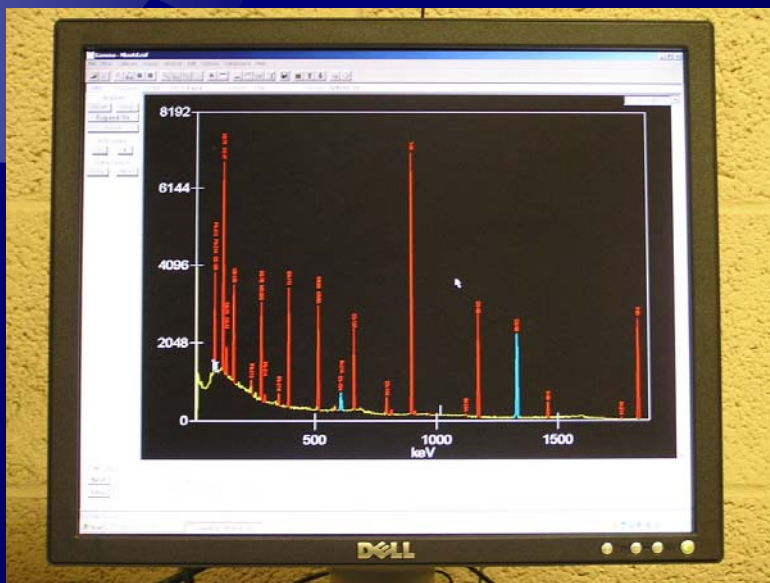


Data acquisition flow sheet

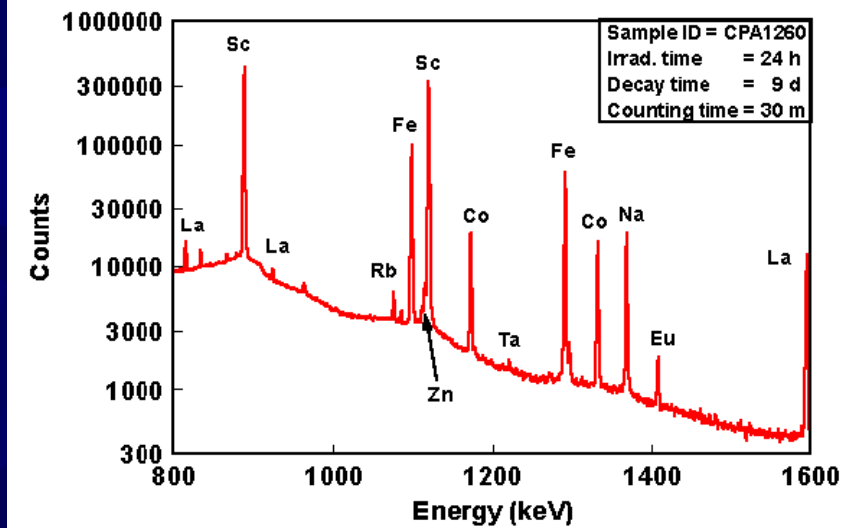
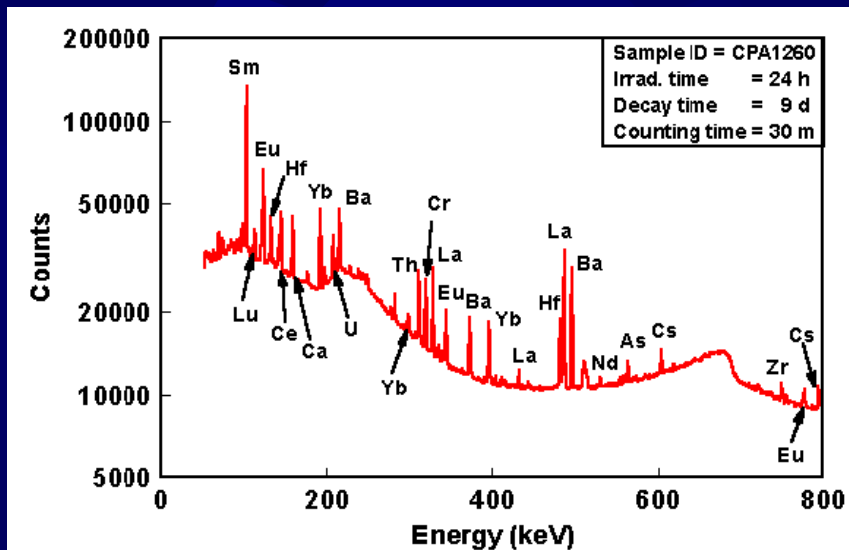




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Gamma ray spectrum for a multi element sample

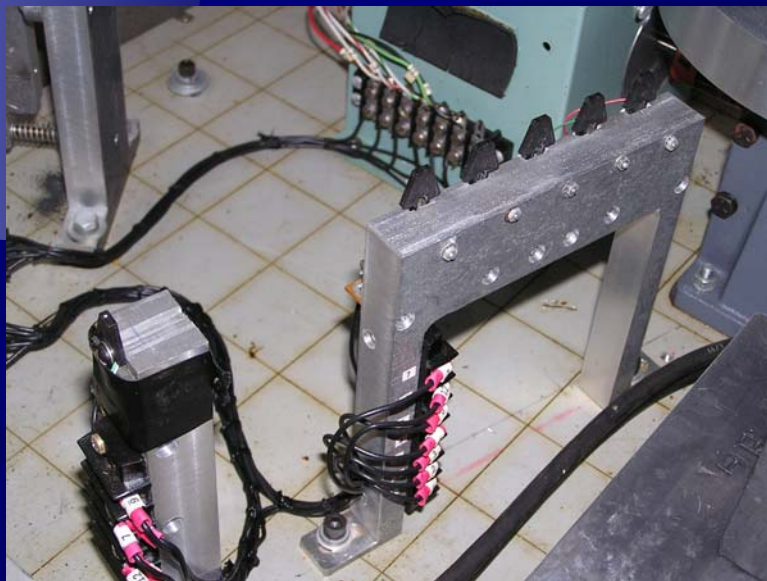




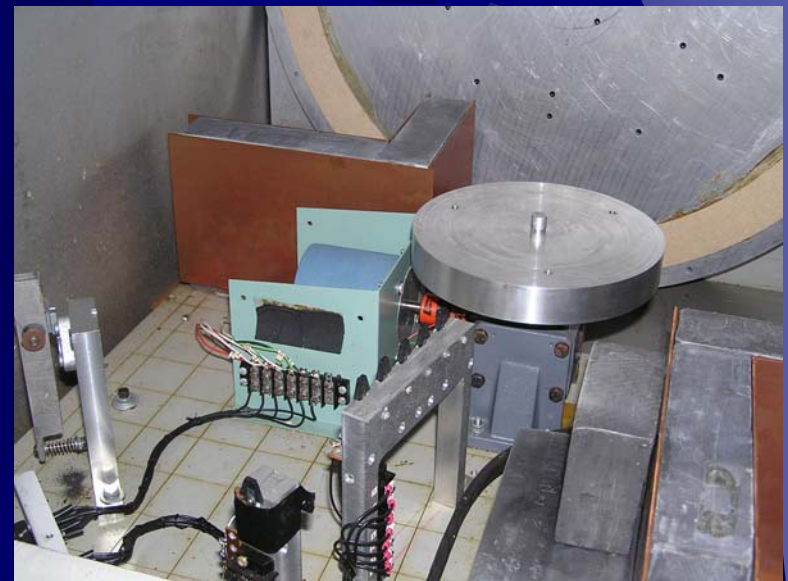
8 cm steel cave



Pb and Cu shielding in detector well



Sensor array for automated sample changer



Stepper motor and drive for sample changer turntable



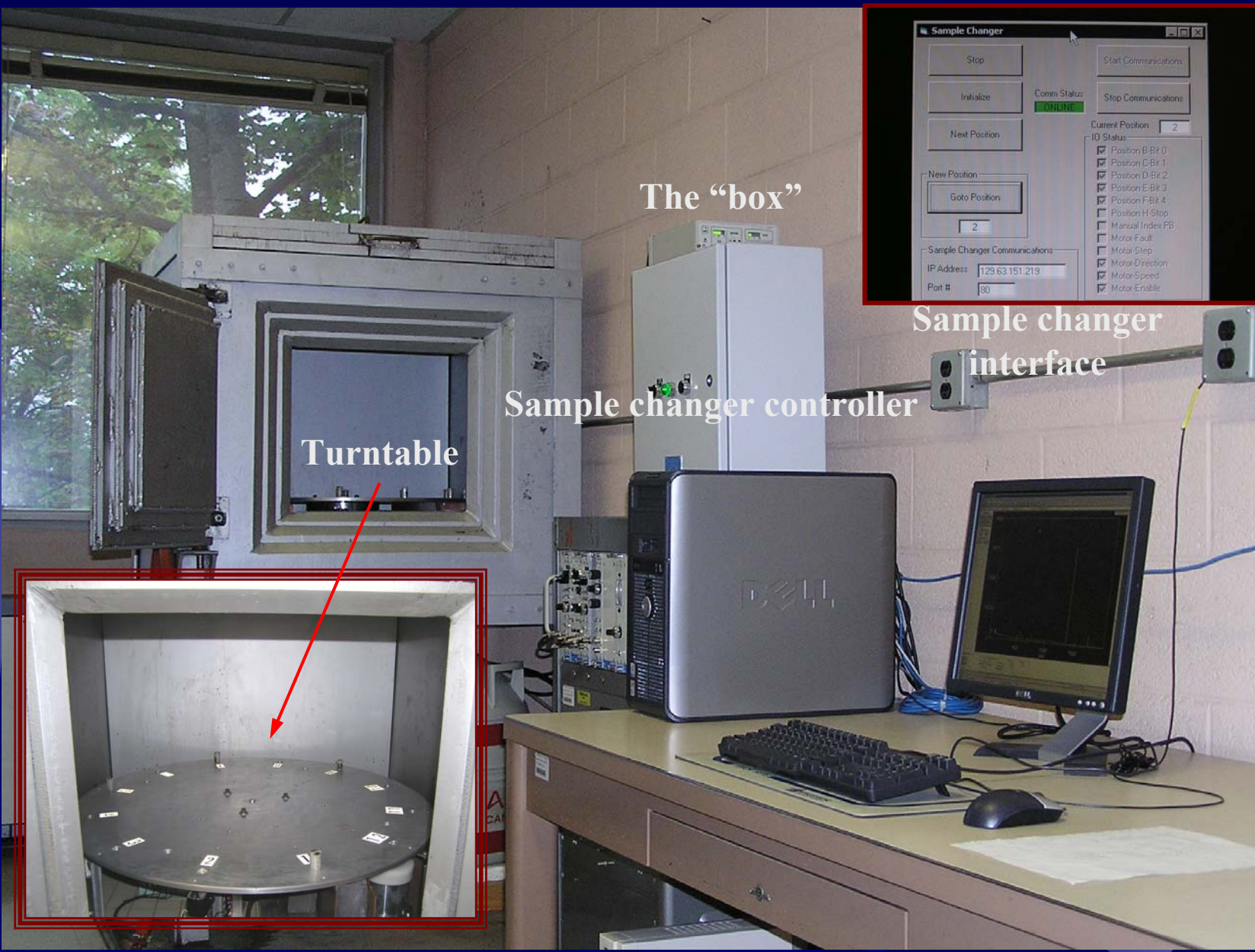
BEGe detector



Detector positioned in shielded well

**All components in place.
Turntable leaning against
back of cave**





The "box"

Sample changer interface

Sample changer controller

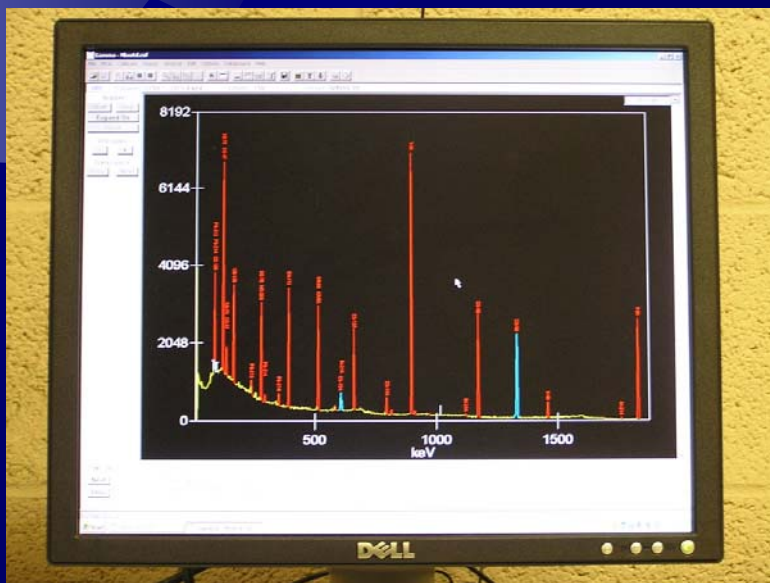
Turntable



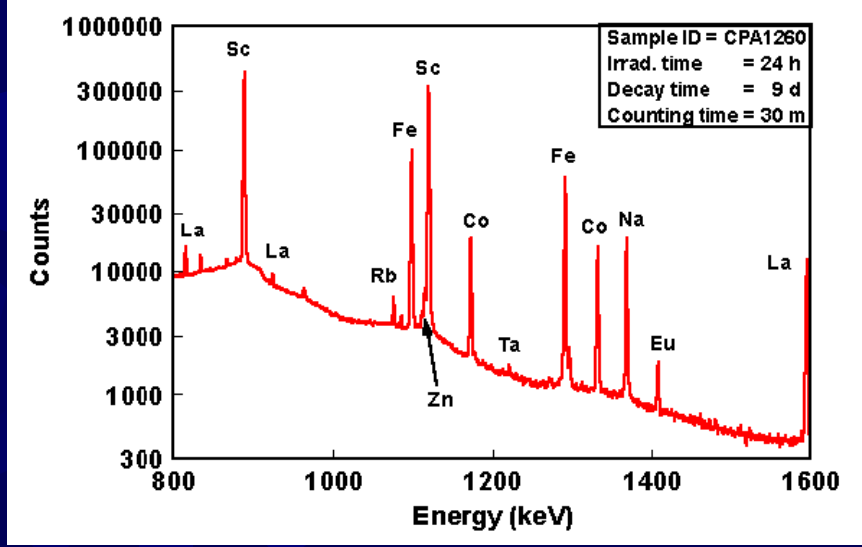
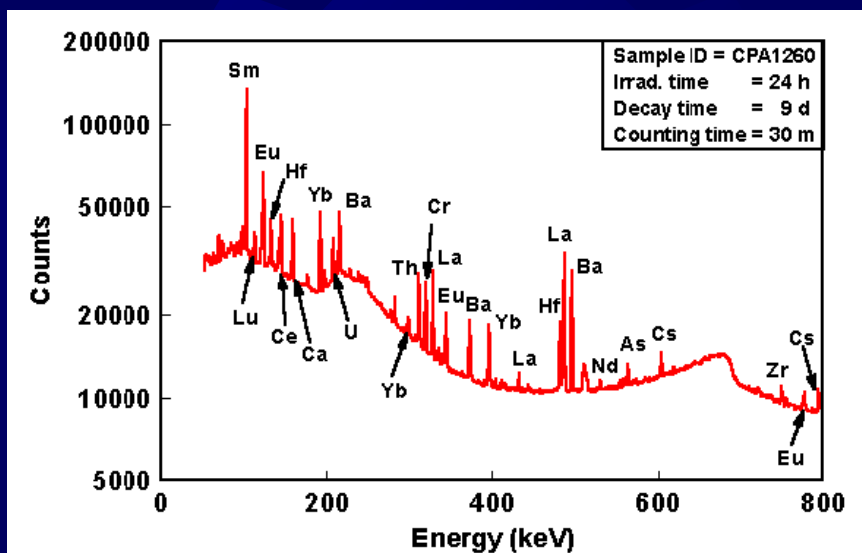
The "box" combines all the spectroscopy and MCA functions – HV to detector, spectroscopy amplifier, ADC, MCA.



UML INAA Lab



Gamma ray spectrum for a multi element sample



Factors to be considered in INAA

- Corrections for inter-element interferences
- Flux monitoring
- Decay corrections to some initial time t and for decay during counting
- Fission product corrections if the sample contains significant U
- Selection of appropriate standards
- Selection of optimum decay times prior to counting. Function of half-lives of elements of interest
- Geometry considerations

INAA Analysis Scheme

- **Irradiate sample (thermal neutrons)**
- **Count sample 5 to 10 days after irradiation to determine short-lived isotopes**
- **Count sample 4 to 8 weeks after irradiation to determine long-lived isotopes**
- **Calculate concentrations after applying decay, interference, fluence, and fission-product corrections.**

Detection limits (DL) for elements that can be determined by INAA

DL (nanograms)	Elements
0.01-0.1	Au, Eu, Ho, Ir, Sm, Lu
0.1-1	Ag, As, Co, Cs, Hf, La, Sb, Sc, Se, Ta, Tb, Th, Tm, U, W, Yb
1-10	Ba, Br, Ce, Cr, Gd, Mo, Na, Nd, Ni, Rb, Sr, Zn, Zr
10-100	K
100-1000	Fe

Advantages of INAA

- Can analyze a large number of elements simultaneously
- Very low detection limits for many elements
- Small sample sizes (1 – 200 mg)
- No chemical preparation
- Nondestructive. The material is available for other analytical techniques
- Relatively low entry cost (~\$60,000) compared to other high sensitivity analytical methods

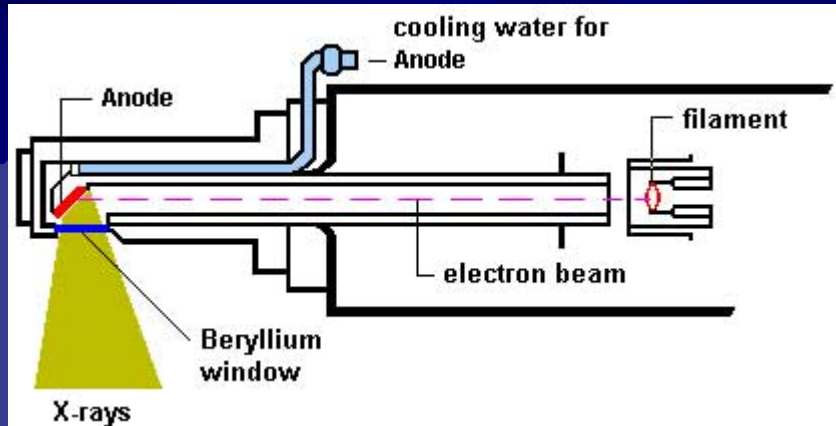
Major Disadvantage of INAA

Can't analyze for all elements of interest. Partner with X-ray fluorescence spectrometry (XRF)

Principles of X-ray Fluorescence Analysis (XRF)

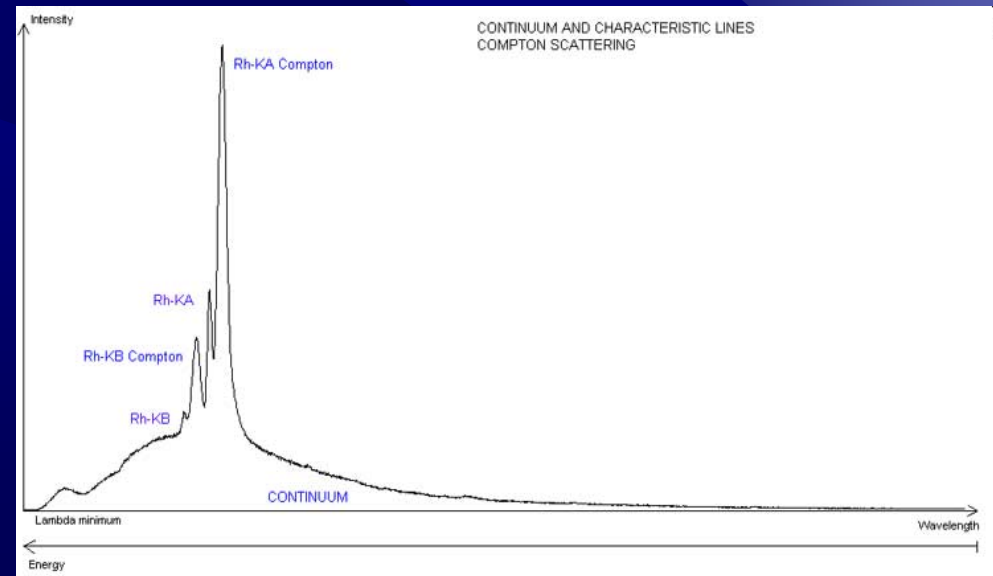


An electron beam impinges on an anode generating X-rays. Rhodium is frequently used for the anode, but other elements are used depending on the type of analysis.

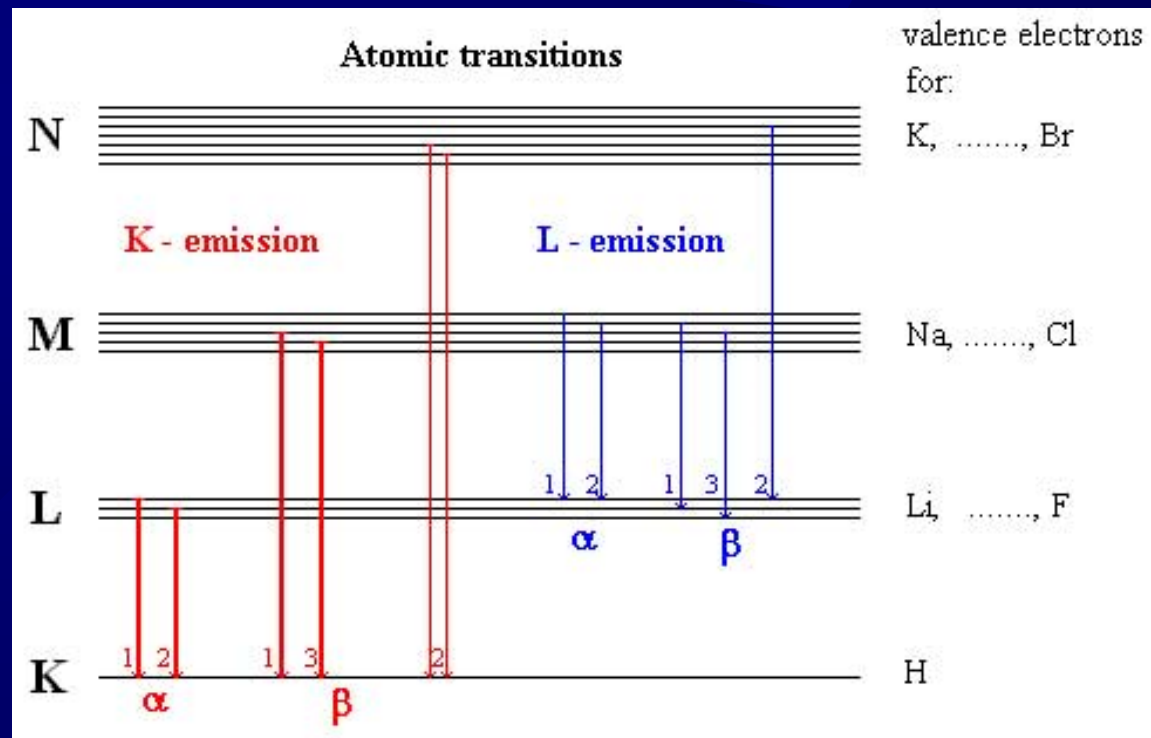


Design of an x-ray tube.

Emitted energy consists of the characteristic X-rays for the anode material plus the continuum.



X-rays from the tube impinge on a sample. The energy is transferred to the sample and electrons are removed from the innermost shells of the atoms. The energy of the resulting x-rays is used to identify the element(s) and the intensity of the emitted x-rays can be used to determine the abundance of the element(s).

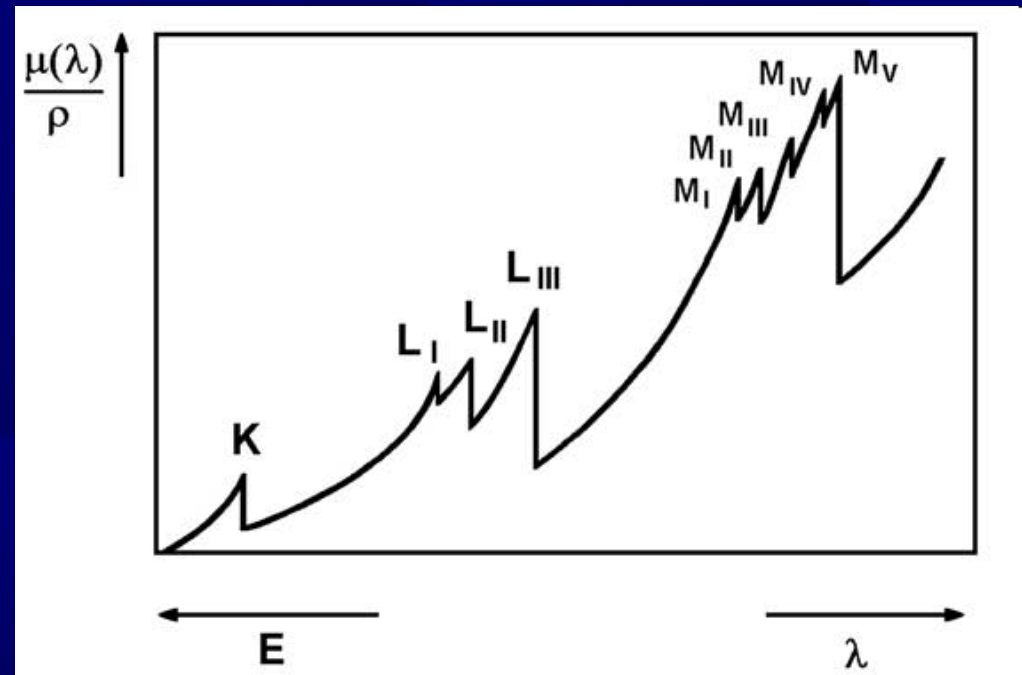


X-rays are absorbed when they enter the sample material. The absorption is a function of the atomic number of the absorber element and the energy of the X-ray quanta. The mathematical relationship is

$$\mu / \rho = \text{mass attenuation coefficient}$$

The mass attenuation coefficient has the dimension [cm²/g].

X-ray absorption varies as a function of energy and the mass attenuation coefficient. If an X-ray quanta has a level of energy that is equivalent to the binding energy of an atomic shell electron in an appropriate shell, it is then able to transfer all its energy to this electron and displace it from the atom. In this case, absorption increases sharply.

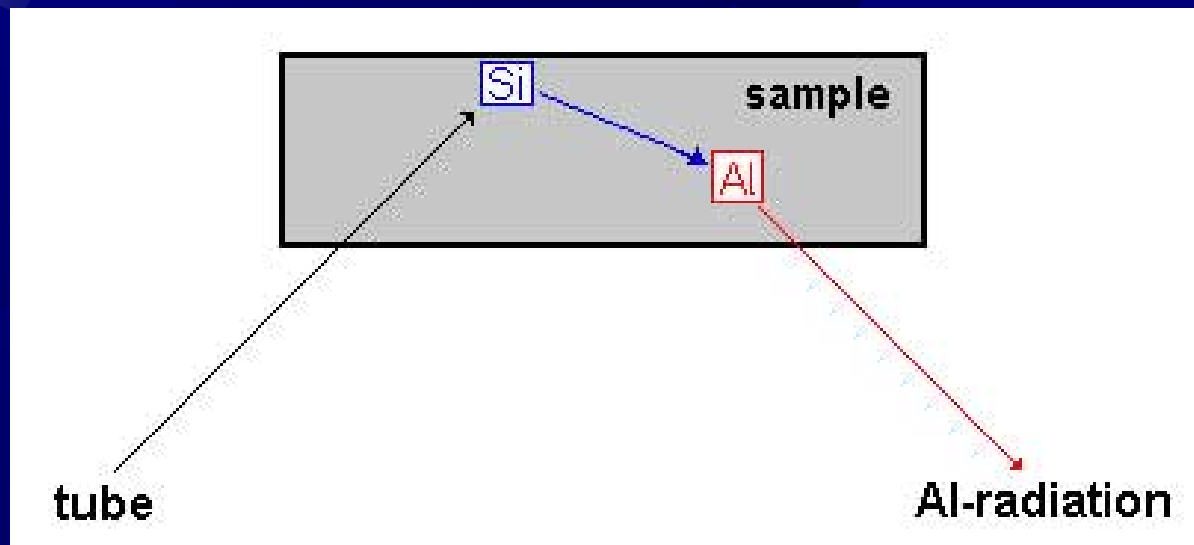


Corrections for absorption are applied by either measuring the Compton scattering or calculating the absorption coefficient from the chemistry of the sample.

Secondary enhancement, i.e. those X-ray quanta that are produced as a result of the effect of the sample elements' absorbed radiation, is closely linked to produced X-rays' absorption in the sample.

Example:

A **Si $K\alpha$** quantum is produced in a sample by the effect of an X-ray tube's radiation. Inside the sample, it can be absorbed again by transferring its energy to an Al K electron. This can then emit an X-ray quantum itself. The silicon radiation thus contributes to the X-ray emission of the aluminum. This is referred to as **secondary enhancement**. Corrections must be applied for this effect.



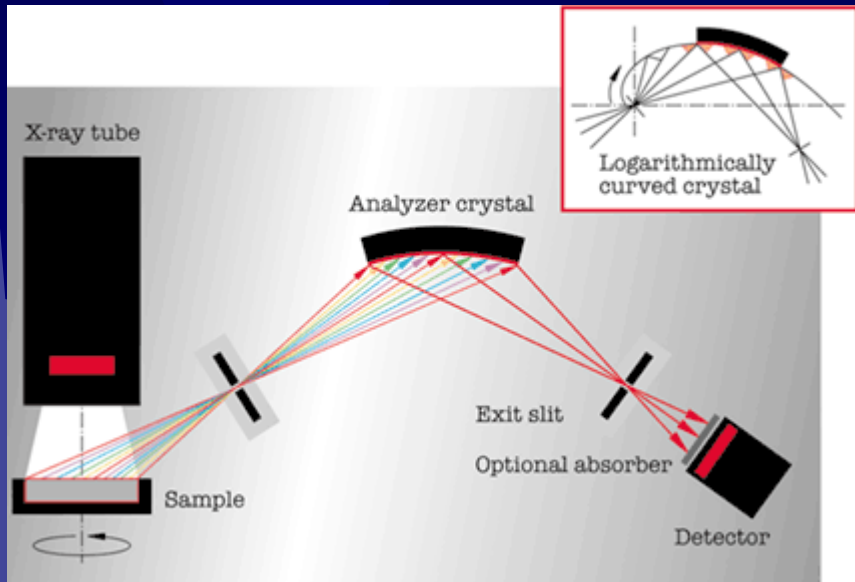
Emitted X-rays are diffracted by a crystal (Bragg's Law once again) to a detector which measures the x-ray energy.

Crystal types

Crystal	Name	Element Range	2d-value (nm)
LiF(420)	Lithium fluoride	\geq Ni $K\alpha_1$	0.1801
LiF(220)	Lithium fluoride	\geq V $K\alpha_1$	0.2848
LiF(200)	Lithium fluoride	\geq K $K\alpha_1$	0.4028
Ge	Germanium	P, S, Cl, Ar	0.653
InSb	Indium antimonide	Si	0.7481
PET	Pentaerythrite	Al - Ti, Kr - Xe, Hf - Bi	0.874
ADP	Ammonium dihydrogen phosphate	Mg	1.064
TIAP	Thallium biphthalate	F - Na	2.576
XS-CEM	Specific Structure	Al - S	2.75
XS-55	Multilayer [W/Si]	N - Al, Ca - Br	5.5
XS-N	Multilayer [Ni/BN]	N	11.0
XS-C	TiO ₂ /C	C	12.0
XS-B	LaB ₄ C	B (Be)	19.0

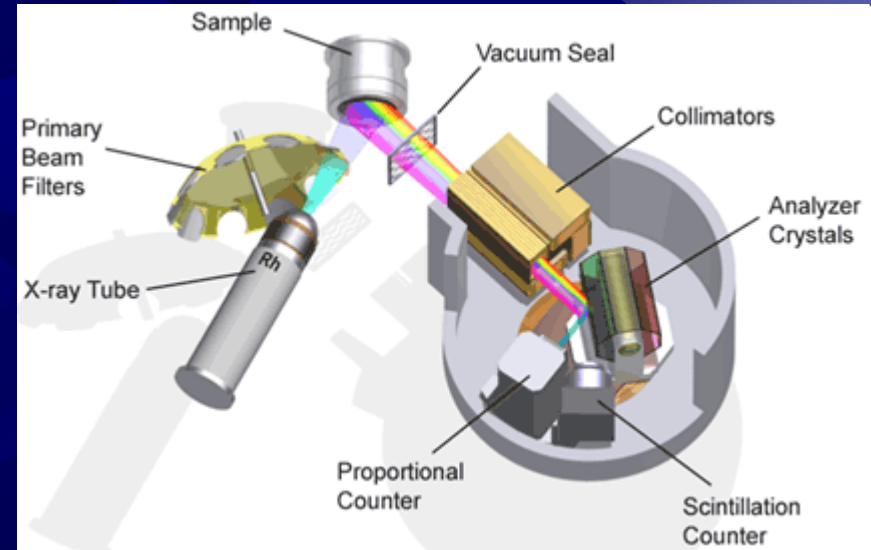
Elemental abundances are determined, following corrections for mass absorption and secondary enhancement, by comparison to appropriate standards.

Types of X-ray Spectrometers



Multichannel spectrometer. The concentrations for a number of elements can be determined at the same time. Logarithmically curved crystal directs specific wavelengths to detectors.

Sequential spectrometer. Element concentrations are determined sequentially by moving the analyzer crystal(s) to achieve the proper solution to the Bragg equation for a particular analytical wavelength.



Elements analyzed by combined INA-XRF Analysis

INA	XRF	INA	XRF	INA	XRF	INA	XRF	INA	XRF
<i>Na</i>	<i>Na</i>	<i>Cr</i>	Cr	Rb	<i>Rb</i>	<i>Nd</i>	Nd	<i>Ta</i>	
	<i>Mg</i>	Mn	<i>Mn</i>	Sr	<i>Sr</i>	<i>Sm</i>		W	
	<i>Al</i>	<i>Fe</i>	<i>Fe</i>		<i>Y</i>	<i>Eu</i>		<i>Au</i>	
	<i>Si</i>	<i>Co</i>	Co	Zr	<i>Zr</i>	<i>Gd</i>			<i>Pb</i>
	<i>P</i>	<i>Ni</i>	<i>Ni</i>		<i>Nb</i>	<i>Tb</i>		<i>Th</i>	Th
K	<i>K</i>		<i>Cu</i>	<i>Sb</i>		<i>Ho</i>		<i>U</i>	
	<i>Ca</i>	<i>Zn</i>	<i>Zn</i>	<i>Cs</i>		<i>Tm</i>			
<i>Sc</i>			<i>Ge</i>	<i>Ba</i>	<i>Ba</i>	<i>Yb</i>			
	<i>Ti</i>	<i>As</i>		<i>La</i>	La	<i>Lu</i>			
	<i>V</i>	<i>Se</i>		<i>Ce</i>	Ce	<i>Hf</i>			

**Bold Italics – preferred method*

Forensics – Source of the Maple Syrup



**Collecting sap the
old fashioned way**

Collecting sap the modern way. Plastic barrels and polyethylene tubing.



Transferring sap to the sugar house



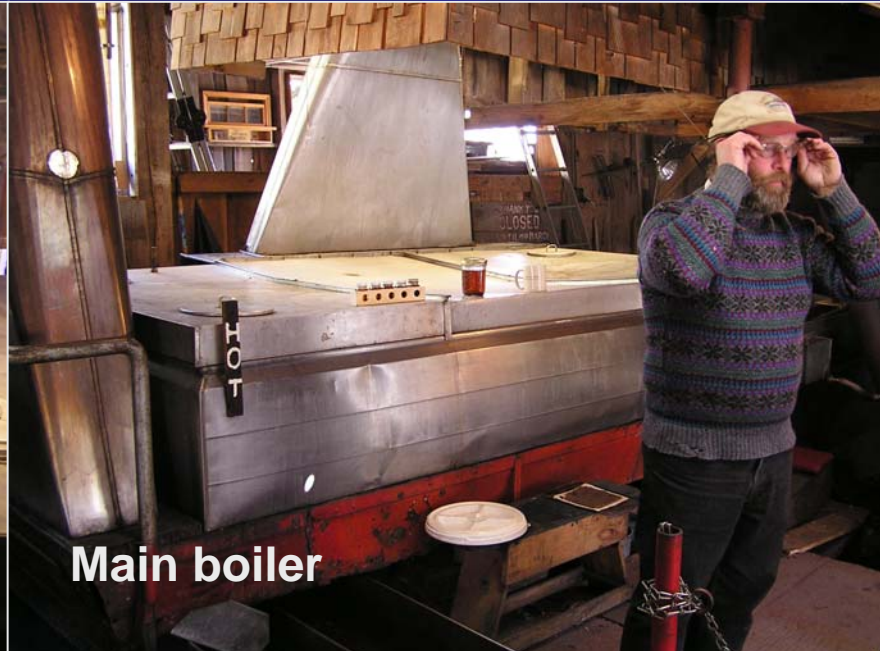
Sap holding vats



Boiling down the sap



Syrup production line



Main boiler

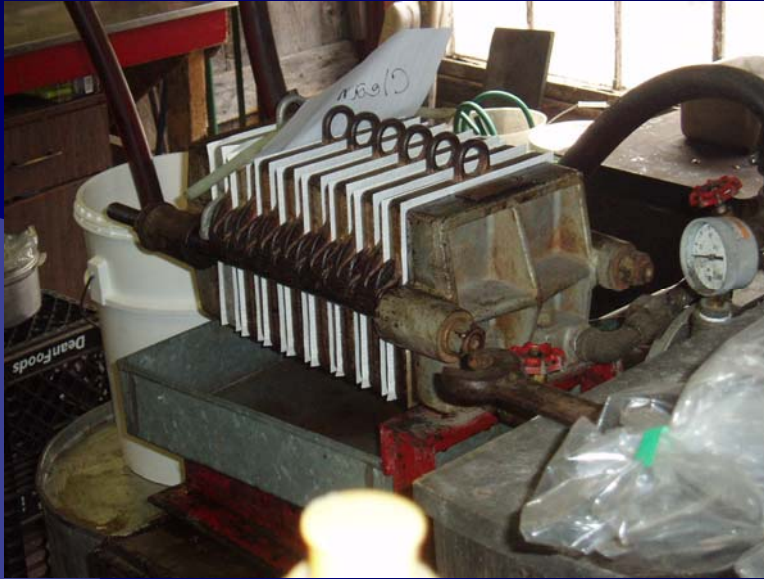


Secondary boiler



Finish boiler

Final step – filtering the product



During the production of maple syrup there are numerous opportunities for trace constituents to be added to the product.

- **In the original sap from trace metals in the soil**
- **During transport**
- **During boiling of the sap – metals from the evaporators**
- **During the final filtration**

These added constituents can be used to “fingerprint” maple syrups from different sources.

Concentrations (ppm) and ratios of trace metals in Maple Syrup

	Newton	Winsor	Parker A	Parker B	W MA	VT	Quebec
Sc	0.010	0.009	0.004	0.008	0.006	0.002	0.030
Cr	0.67	0.71	0.83	nd	0.87	0.136	1.67
Co	0.094	0.064	0.073	0.046	0.057	0.078	0.119
Zn	9.3	13.1	50.6	19.4	76.3	5.5	19.4
Rb	7.5	3.1	10.2	5.7	15.7	7.5	9.0
Sr	28.6	13.7	10.7	nd	8.3	10.5	17.5
As	0.029	0.014	0.022	nd	0.010	0.016	0.016
Sb	0.018	0.010	0.034	0.004	0.010	0.002	0.009
Se	ppb	nd	nd	nd	nd	nd	8.72
Zn/Cr	13.9	18.5	61	nd	88	40	11.6
Rb/Cs	642	363	433	nd	175	356	419
Ba/Sr	0.59	0.18	0.76	nd	1.29	2.26	0.37
As/Sb	1.59	1.50	0.64	nd	2.24	8	1.91

Trace metals in nanotech materials – Respirable particles

Element	Carbon Black	Fullerene	Nano TiO ₂	CNT	Silica	Nano alumina	
Fe	25.9	11.7	24.1	2441	450	18.6	ppm
Sc	0.002	0.003	4.88	nd	0.200	0.028	ppm
Cr	0.303	0.099	2.18	536	1.68	0.714	ppm
Co	0.015	0.024	0.43	19582	0.30	0.030	ppm
Ni	0.3	0.4	nd	317	64	0.2	ppm
Zn	8.26	4.15	32.8	1202	6.45	37.5	ppm
Ba	nd	0.89	52.4	nd	14.8	nd	ppm
Sr	6.0	nd	nd	nd	9.7	nd	ppm
Ce	4.79	3.91	1.56	nd	4.60	3.36	ppm
Zr	nd	nd	13743	1305	32.2	134	ppm
Ta	0.010	0.017	61.9	nd	0.048	0.008	ppm
As	0.050	0.010	16.3	0.58	0.212	0.022	ppm
Mo	nd	nd	1.6	415	nd	nd	ppm
Sb	0.020	0.002	321	16.27	0.089	1.23	ppm
W	0.030	0.004	11.96	0.46	0.034	27.9	ppm
Au	47.5	0.03	99.7	1.29	nd	nd	ppb
Se	nd	0.66	nd	nd	9.5	23.5	ppb



**Location map
for Tanzania
National
Parks**

Serengeti plains

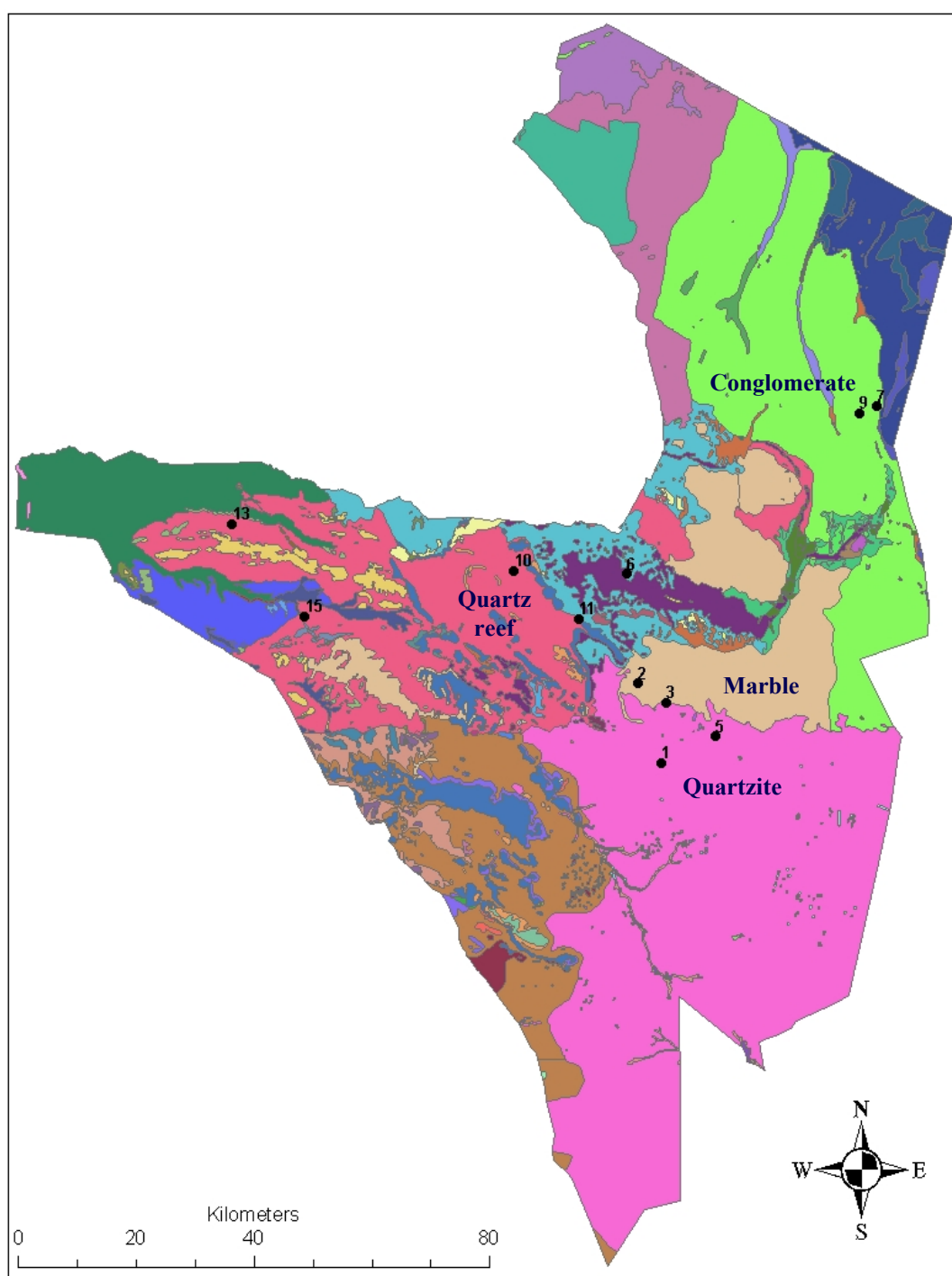


Serengeti Grasses

Digitaria

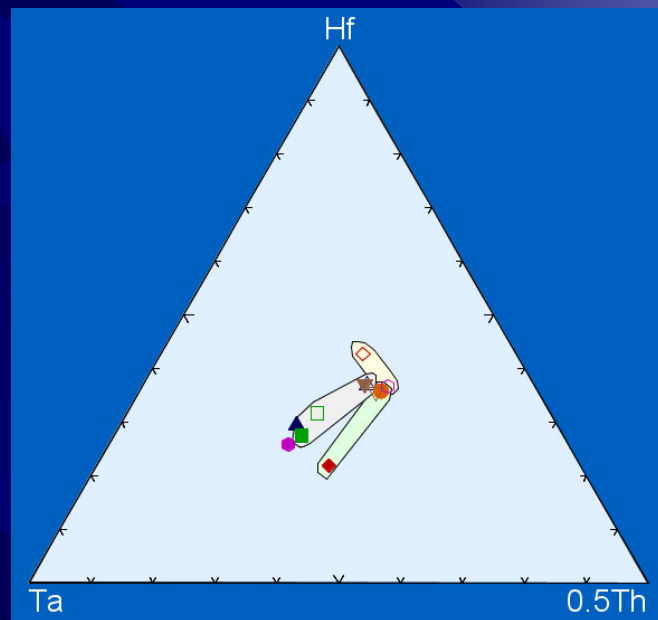
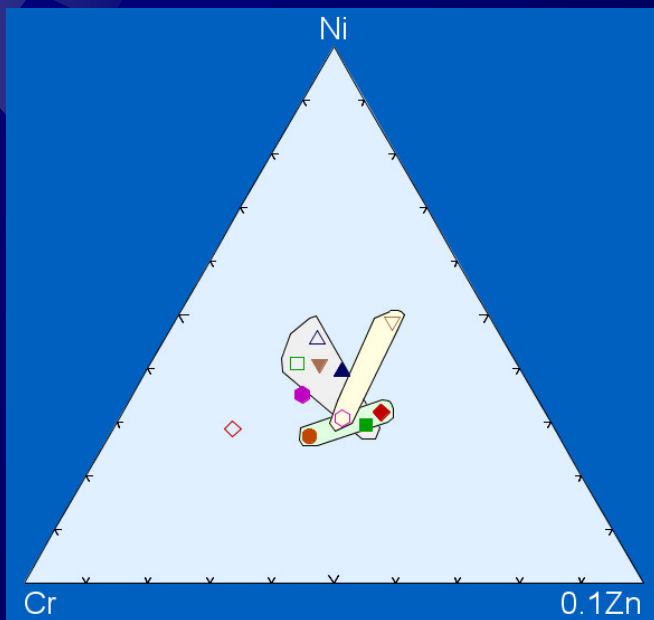
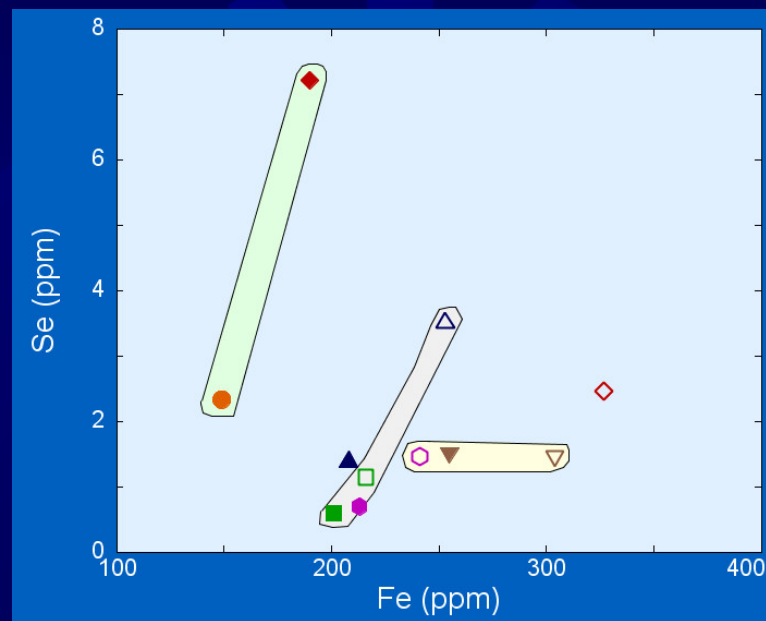
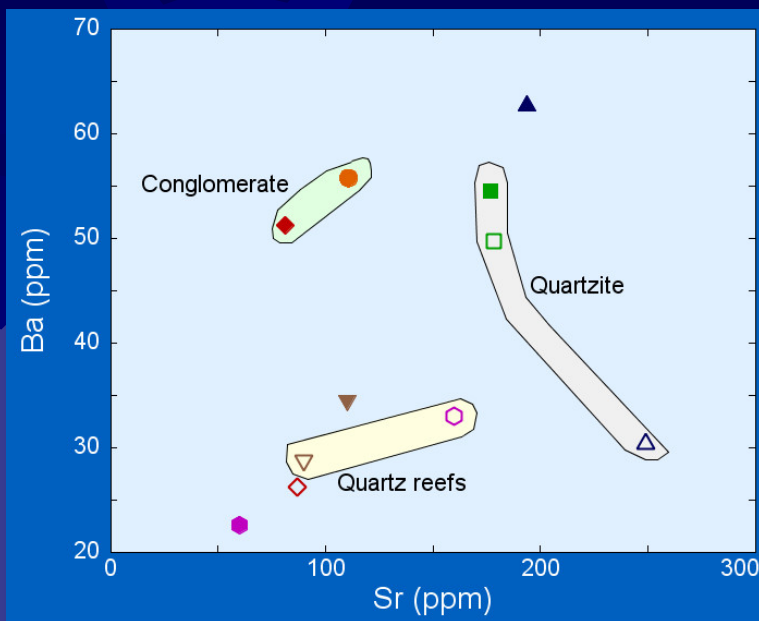
Sporobolus

Themeda



Sample Locations and Geology

Trace element distributions for grasses from geographic areas with different bedrock geology.

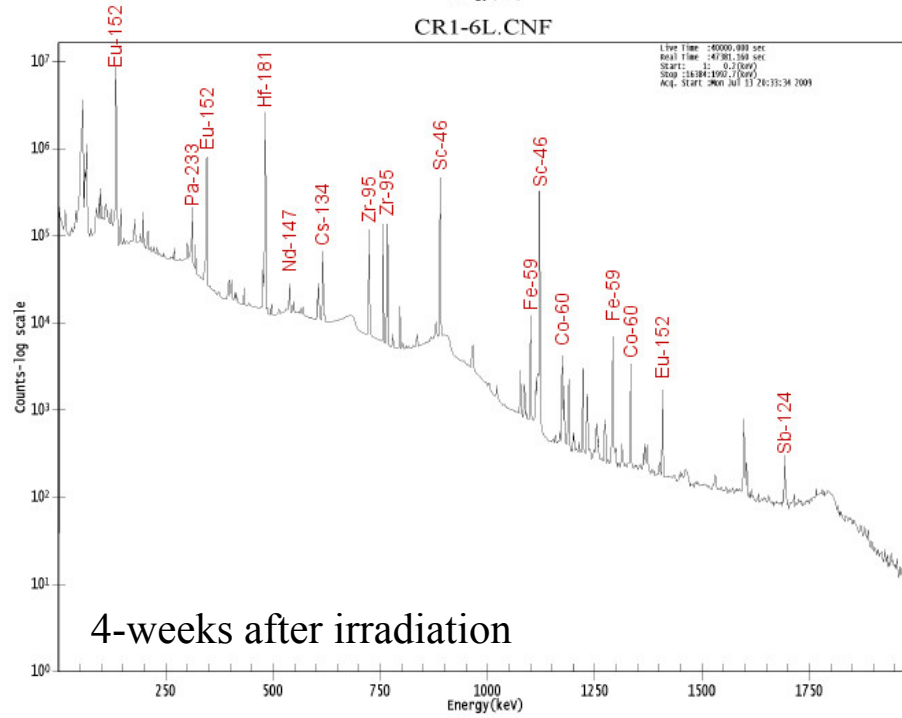
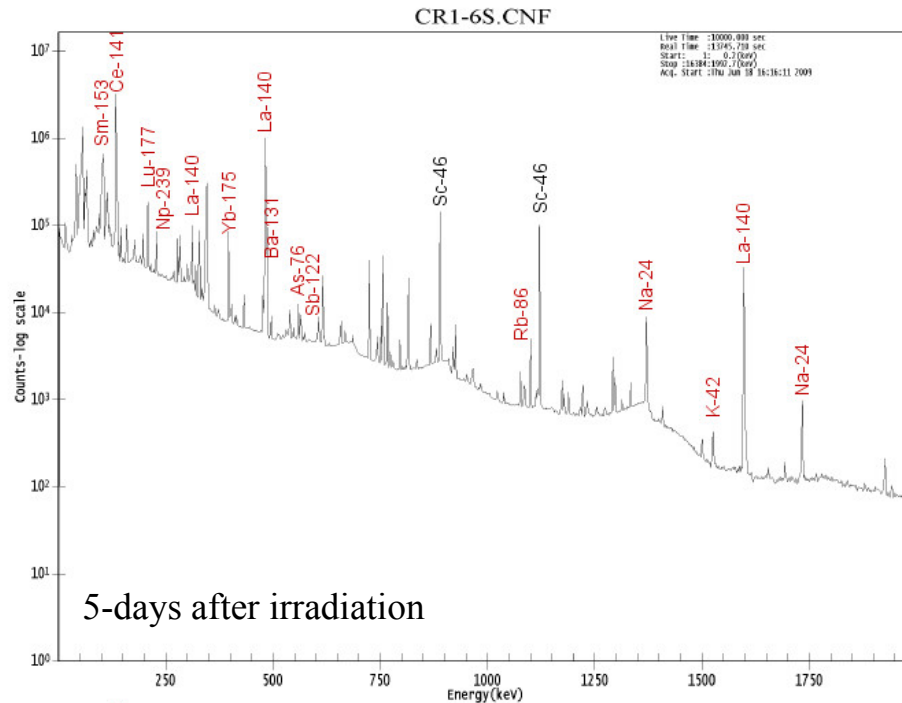


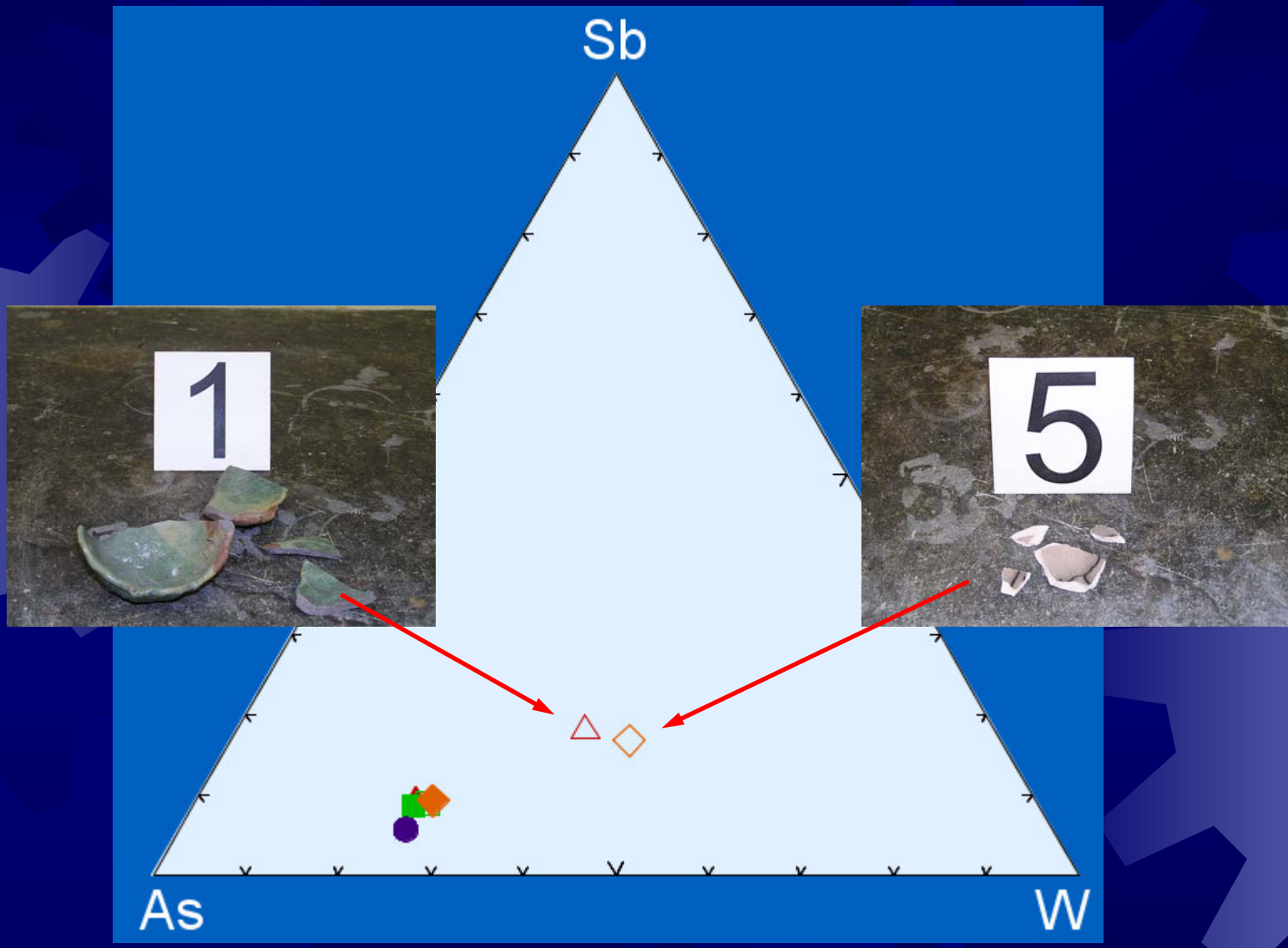
Summary of Materials Used in Glazes

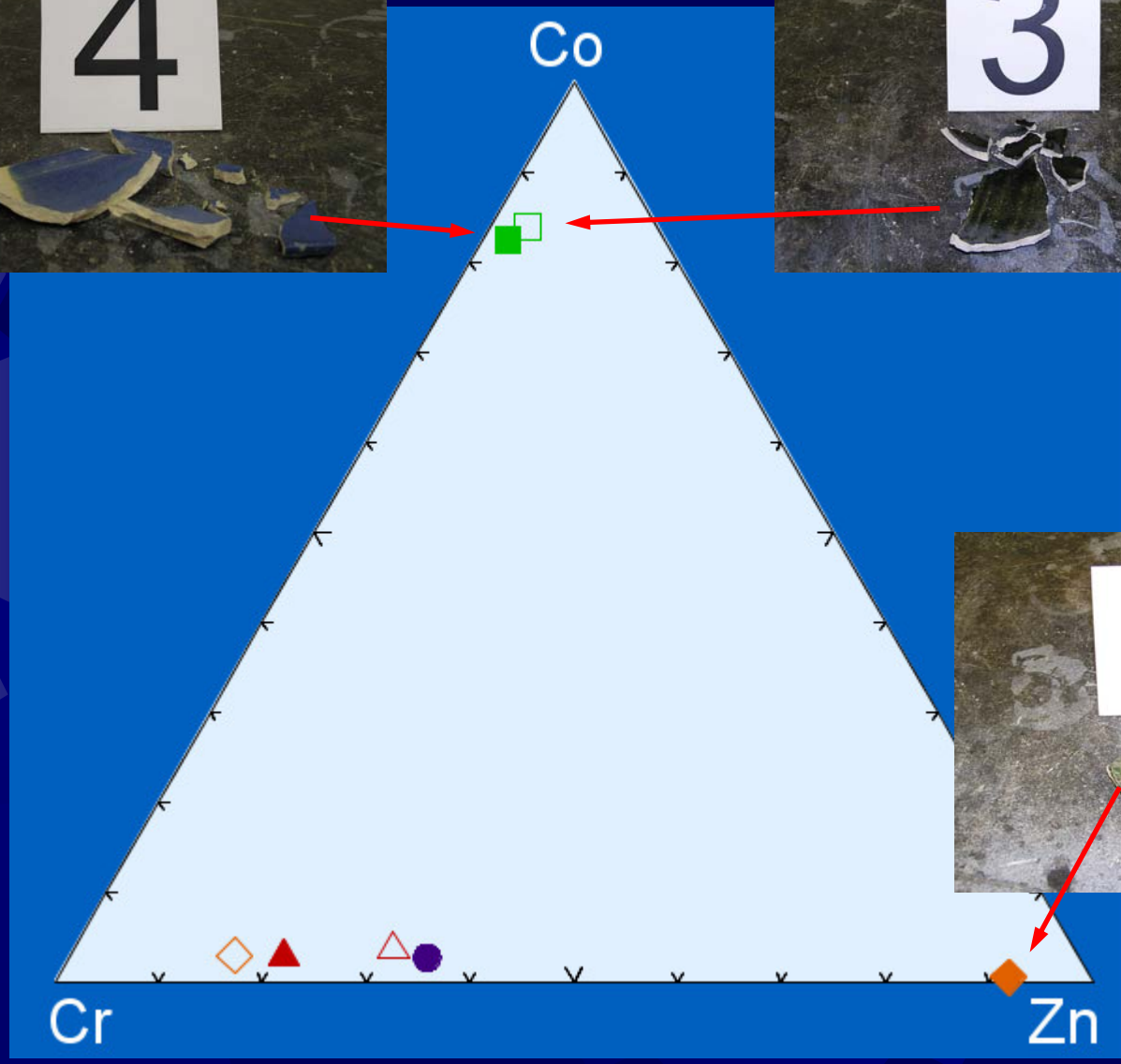
Material	Chemistry
Bentonite	$((\text{Na},\text{Ca})_{0.33}(\text{Al},\text{Mg})_2(\text{Si}_4\text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O})$
Cryolite	Na_3AlF_6
Dolomite	$\text{CaMg}(\text{CO}_3)_2$
Epsom salts	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
Fluorspar	CaF_2
Gerstley borate	$2\text{CaO} \cdot 3\text{B}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$
Kaolin (Kaolinite)	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$
Lepidolite	$\text{K}(\text{Li},\text{Al})_3(\text{Al},\text{Si})_4\text{O}_{10}(\text{F},\text{OH})_2$
Lithium carbonate	LiCO_3
Nepheline syenite	Various Na-K-Al silicate minerals
Potash feldspar (K-spar)	KAlSi_3O_8
Silica (Quartz)	SiO_2
Soda feldspar (Albite)	$\text{NaAlSi}_3\text{O}_8$
Whiting (Calcite)	CaCO_3
Wollastonite	CaSiO_3
Zircopax (Zircon)	ZrSiO_4
Colorant Oxides	
Cobalt	Co
Copper carbonate	CuCO_3
Hematite	Fe_2O_3
Rutile	TiO_2

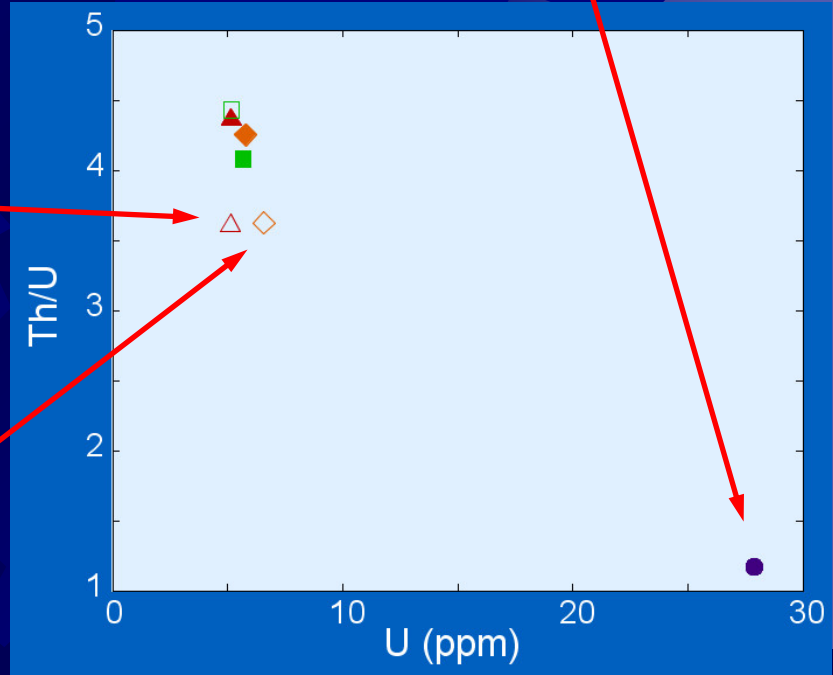
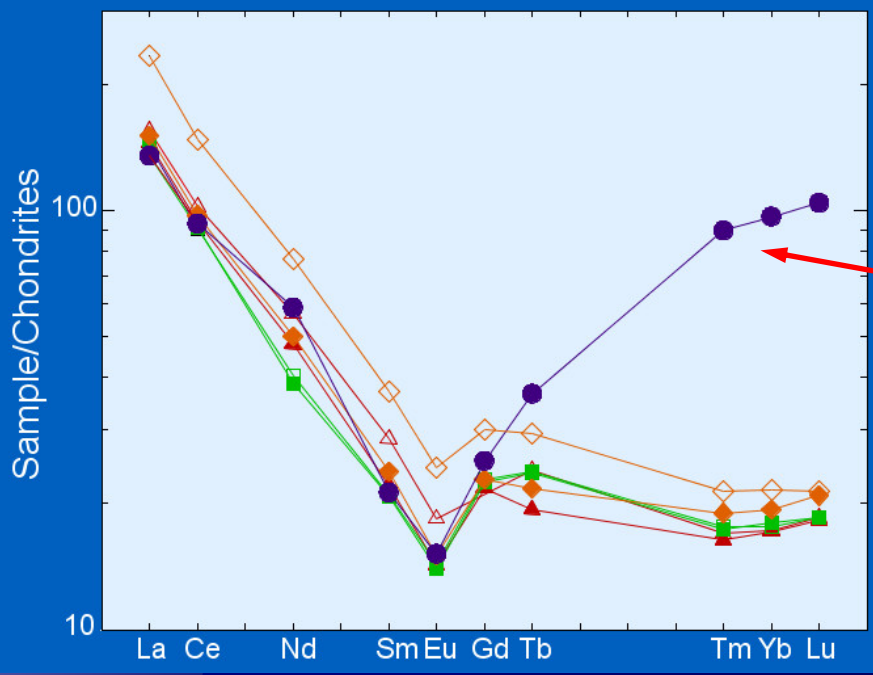


Gamma ray spectrum for Ceramic 6









Trace elements and Forensic Science

The important point is that for numerous reasons similar materials can have different trace element concentrations. These differences can potentially be used to distinguish between items in a class and either match or eliminate the item.

For example: The grass on a suspect's shoe is the same species as that found at a crime scene. But different trace element content for the grass at the crime scene compared to that on the suspect's shoe indicates that the grass on the shoe did not come from the crime scene.

Acknowledgements

Some of the graphics and text used in this presentation are from the Bruker-AXS web site.