Non Scattering Techniques I

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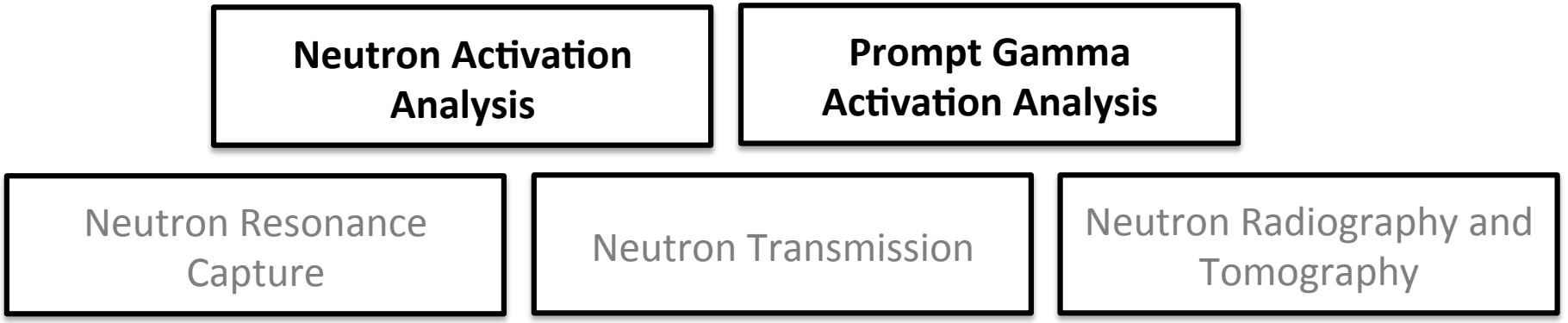
Non-Scattering Techniques



Neutron Activation Analysis

Qualitative and quantitative multi-element analysis of major, minor, and trace elements

Neutron Activation Analysis

Qualitative and quantitative multi-element analysis of major, minor, and trace elements

- Qualitative and Quantitative analysis
  - Qualitative → elemental identification
  - Quantitative → measurement of the values of concentrations

Neutron Activation Analysis

Qualitative and quantitative multi-element analysis of major, minor, and trace elements

- Qualitative and Quantitative analysis
- Multi-element analysis: can simultaneously measure up to 30 elements

Neutron Activation Analysis

Qualitative and quantitative multi-element analysis of major, minor, and trace elements

- Qualitative and Quantitative analysis
- Multi-element analysis
- Major, Minor, and Trace element analysis
  - Major: Concentrations > 1%
  - Minor: Concentrations in the range 0.1% to 1.0%
  - Trace : Concentrations < 0.1%

Neutron Activation Analysis

- Applications in archeology, chemistry, geology, medicine, agriculture, environmental monitoring, and forensic science
- NAA is recognized as the reference method of choice when new procedures are being developed or when other methods yield results that do not agree because of its accuracy and reliability
- Approx. 100,000 samples undergo NAA each year

NAA and Archaeology

- **Provenance** Research - link artifacts to their origin based on the unique geochemical signature of the raw material
- **Ancient Technology** - infer technological processes (trace-element composition)
- **Authentication** - verify authenticity or antiquity (trace-element composition)
- **Palaeo-diet and Nutrition** - examine diet and nutritional status of prehistoric populations from bone chemistry

Historical background

1936 Hevesy and Levi discovered neutron activation analysis. Samples containing certain rare earth elements became highly radioactive when irradiated with neutrons

→ Hevesy and Levi recognized the potential for identifying elements present in samples through measurement of different radiations and half-lives of the radioactive elements

George de Hevesy: 1885-1966

Hilde Levi: 1909 - 2003

Historical background

- 1950s- 1960s Construction of nuclear reactors

  → neutron fluxes sufficient to allow sensitivities for NAA at levels of interest to solving real analytical problems

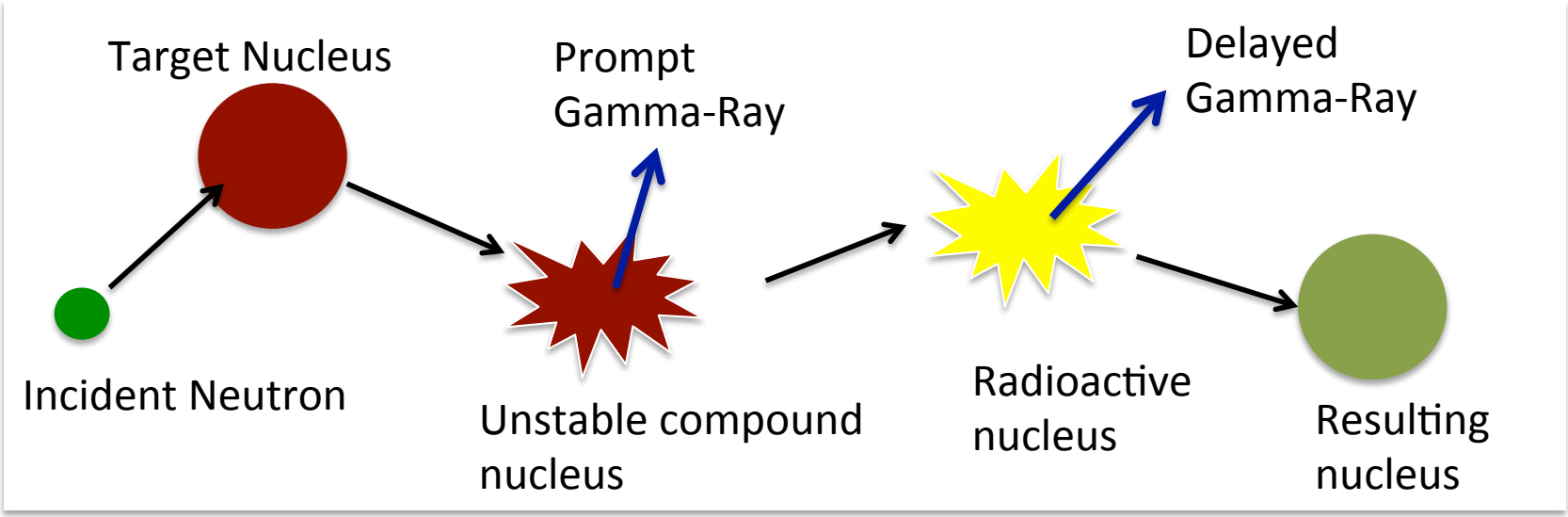
- 1954 Robert Oppenheimer sees the potential of NAA in archaeology. He suggested its use to Dodson and Sayre of Brookhaven National Laboratory as a possible way to establish the provenance of archaeological finds

Historical background

- 1970s-1980s Many archaeologists use NAA to determine the provenance of artifacts
- 1970s-1980s University of Michigan, University of Toronto, National Institute of Standards and Technology, University of Missouri, and many others develop NAA laboratories
- 1990s NAA becomes the technique of choice for provenance research

Principles of the method

- NAA involves the **irradiation** of a sample by **neutrons** to make the **sample radioactive**. **After irradiation**, the **gamma-rays** emitted from the radioactive sample are measured to determine the amounts of different elements in the sample



Neutron sources

- Nuclear Reactors: high neutron flux → source of choice for NAA

Neutron sources

- Nuclear Reactors
- Neutron Spallation Sources

Neutron sources

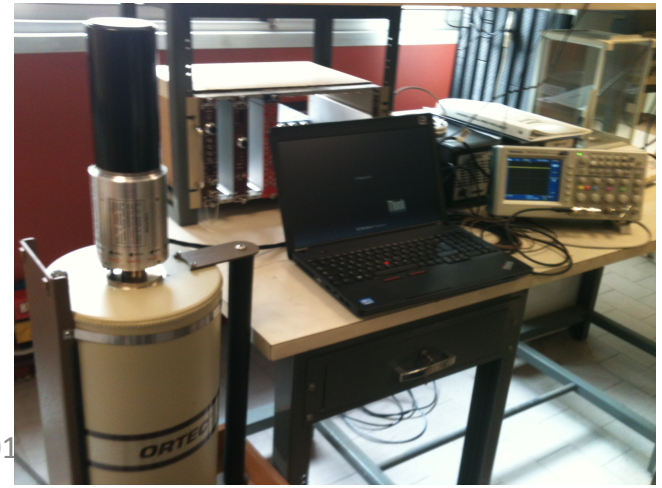
- Nuclear Reactors
- Neutron Spallation Sources
- Radioisotopic neutron sources

  An alpha emitting isotope is mixed with berillium. This generates neutrons by the $\alpha + {}^{9}Be -> {}^{12}C + n$ reaction

  Prons: cheap, easily available Cons: Weak source

Detection system

- Measure gamma-ray activity of an irradiated sample → Gamma-ray spectrometer
- Gamma-ray spectrometer consists of
  1. Gamma-ray detector
  2. Electronics
  3. Computer



Gamma-ray detector

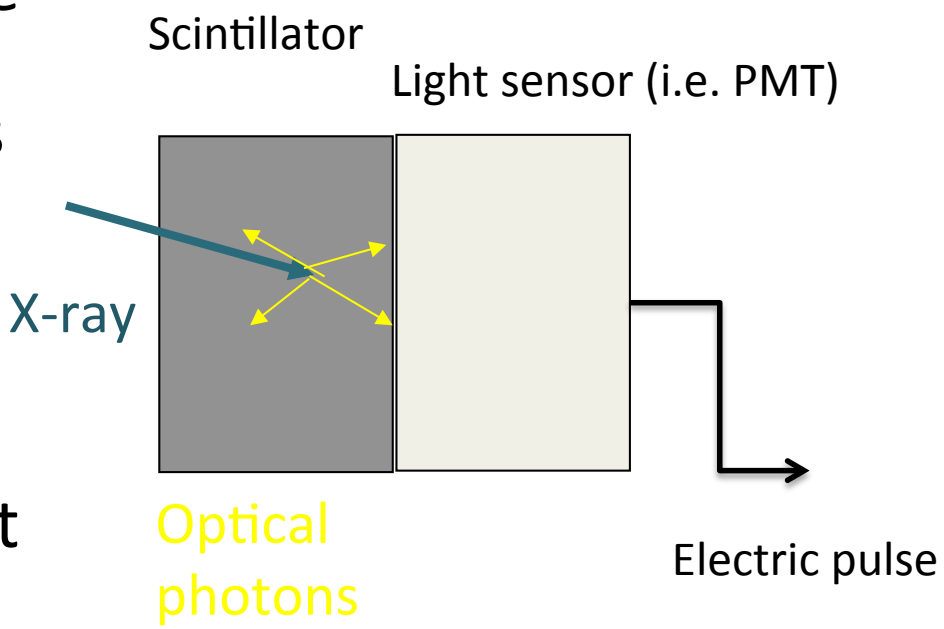
- Gamma-ray detector converts energy of gamma radiation into an electrical signal

- The two major types of gamma detectors used in Neutron Activation Analysis are
  - Semiconductors : HPGe, CdTe
  - Scintillators : NaI(Tl)

Reference: MIT, IAP 12-091 Session 1, 2005, ILA PILLALAMARRI

Gamma-ray detector

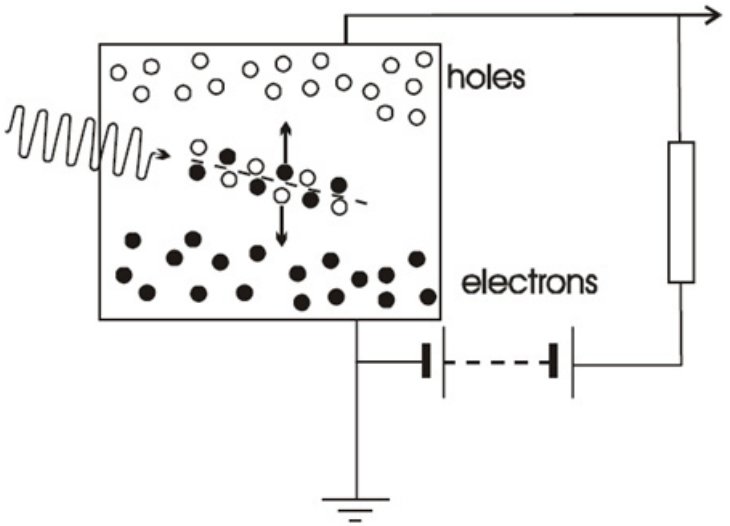
- <u>Scintillation detector:</u>
  scintillator + light sensor
- The scintillator converts the energy of the gamma radiation into light photons
- The light sensor converts the light photons striking onto it into electric pulses.
- The electrical signal is proportional to the incident radiation energy.



Reference: MIT, IAP 12-091 Session 1, 2005, ILA PILLALAMARRI

Gamma-ray detector

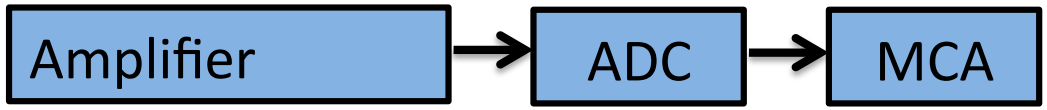
- Semiconductor detectors: Photons incident on the crystal create electrons and holes
- An electric field is created by applying high voltage to the electrodes mounted on opposite sides of the detector crystal.
- The charge carriers get attracted to the electrodes of opposite polarity because of the electric field.
- The charge collected at the electrodes is proportional to the energy lost by the incident radiation.



Reference: MIT, IAP 12-091 Session 1, 2005, ILA PILLALAMARRI, NSEP

Electronics

- Amplifier shapes and amplifies the pulse
- Analog to Digital Converter (ADC) digitizes the signal
- Multi Channel Analyzer (MCA) sorts the digitized result in bins



Data Analysis

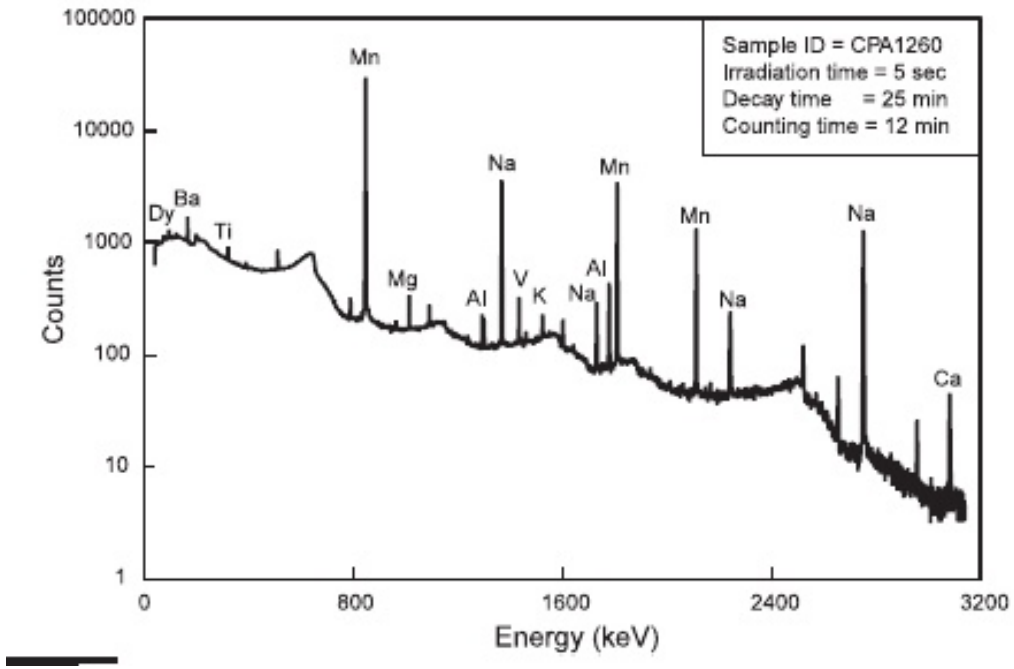
1. Identify the isotopes in the γ-ray spectrum
2. Determine the elemental concentration

Data Analysis

1. Identify the isotopes in the γ-ray spectrum

Gamma library (Half life, Decay mode, Branching ratio, Emitted radiations of radioactive nuclides)

Identify the nuclides responsible for the peaks in the gamma-ray spectrum



Taken from M D Glascock and H Neff, Meas. Sci. Technol. ***14*** *(2003)*

Data Analysis

2. Determine the elemental concentration
   - Irradiate the sample and a standard of known concentration
   - Measure gamma-ray spectra for both sample and standards
   - Calculate concentrations from measured activity of sample and standard

$$\frac{c_x}{c_{std}} = \frac{W_{std} A_x}{W_x A_{std}}$$

c = concentration of the element in the sample (x) and standard (std)
W = weight of sample (x) and standard (std)
A = activity of sample (x) and standard (s)

Sensitivities

Sensitivity (picograms)	Elements
1	Dy, Eu
1-10	In, Lu, Mn
10-10^2	Au, Ho, Ir, Re, Sm, W
10^2-10^3	Ag, Ar, As, Br, Cl, Co, Cs, Cu, Er, Ga, Hf, I, La, Sb, Sc, Se, Ta, Tb, Th, Tm, U, V, Yb
10^3-10^4	Al, Ba, Cd, Ce, Cr, Hg, Kr, Gd, Ge, Mo, Na, Nd, Ni, Os, Pd, Rb, Rh, Ru, Sr, Te, Zn, Zr
10^4-10^5	Bi, Ca, K, Mg, P, Pt, Si, Sn, Ti, Tl, Xe, Y
10^5-10^6	F, Fe, Nb, Ne
10^7	Pb, S

[Table taken from M. D. Glascock University of Missouri Research Reactor (MURR)]

Sensitivities

- Sensitivities superior to those attainable by other methods: parts per billion or better
- Detect up to 70 elements

-

Sensitivities

- Sensitivities depend on experimental procedure

Irradiation parameters

- neutron flux
  nuclear reactors with their high fluxes of neutrons offer the highest available sensitivities
- irradiation time
- decay time

Measurement conditions

- counting time
- detector efficiency

-

Sensitivities

- Sensitivities depend on experimental procedure and chemical element
    - isotope abundance
    - neutron cross-section
    - half-life

    some nuclei have very long half-life → they decay after months or years (^{28}Al half life=2 min, ^{137}Cs half-life=30y)
    - gamma-ray abundance

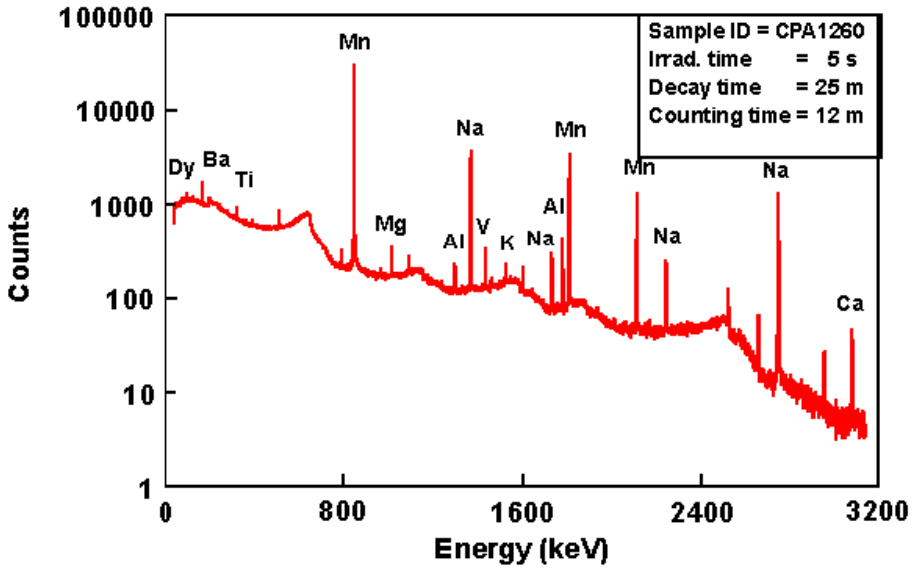
-

Pros

- Selectivity
  - sensitivity for **long-lived radionuclides** suffering from interference by shorter-lived radionuclides → improved by waiting for the short-lived radionuclides to decay
  - sensitivity for **short-lived isotopes** suffering from interference by long-lived radionuclides → improved by reducing the irradiation time and decay time

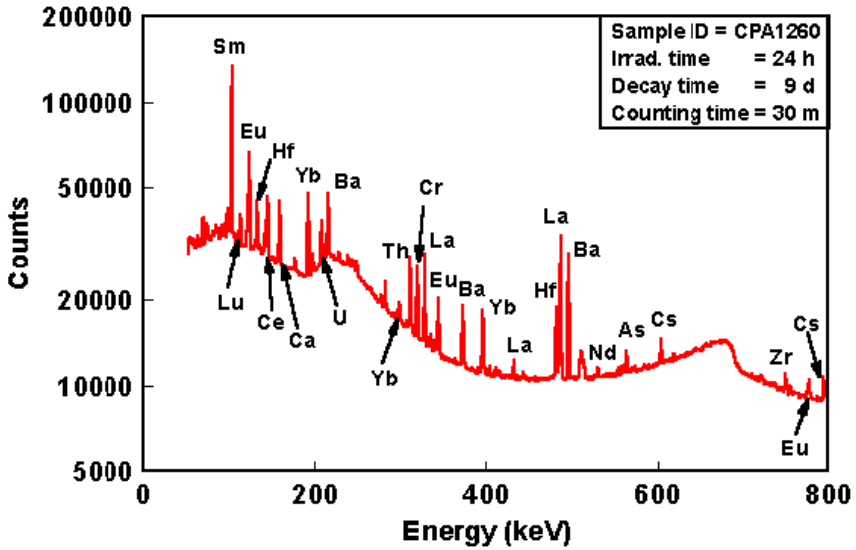
Irradiation time: 5 sec
Decay time: 25 min
Counting time: 12 min

→ short-lived elements



Irradiation time: 24 h
Decay time: 9 days
Counting time: 30 min

→ medium- and long-lived elements



Pottery specimen. Detector: HPGe

Pictures taken from Michael D. Glascock University of Missouri Research Reactor (MURR)

Pros

- Selectivity
- Number of elements

  - Many elements become radioactive when exposed to the neutron flux in a reactor.

  - More than 50 elements can be identified and measured quickly and easily

Pros

- Selectivity
- Number of elements
- Multi-element analysis

  - Measure a large number of elements from isotopes having different activities and half-lives by using different combinations of irradiation and decay times

  - NAA is the only procedure that can simultaneously measure up to 30 elements

Pros

- Selectivity
- Number of elements
- Multi-element analysis
- Highly sensitive

  Many elemental concentrations are measurable in parts per million or parts per billion

Pros

- Selectivity
- Number of elements
- Multi-element analysis
- Highly sensitive
- Elemental analysis

  Elements are determined regardless of their chemical form (free of matrix-effects)

Cons

- Bulk analysis technique

  Whatever is irradiated contributes to the gamma spectrum. It does not provide spatial resolution or imaging capabilities.

Cons

- Bulk analysis technique
- Expensive

  Best sensitivities @ reactors → expensive, not easily available

Cons

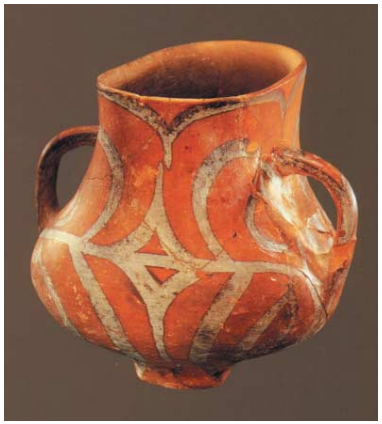
- Bulk analysis technique
- Expensive
- Radioactive

  Samples become radioactive → they must be stored safely in the facility

Is NAA a Non-Destructive technique ?

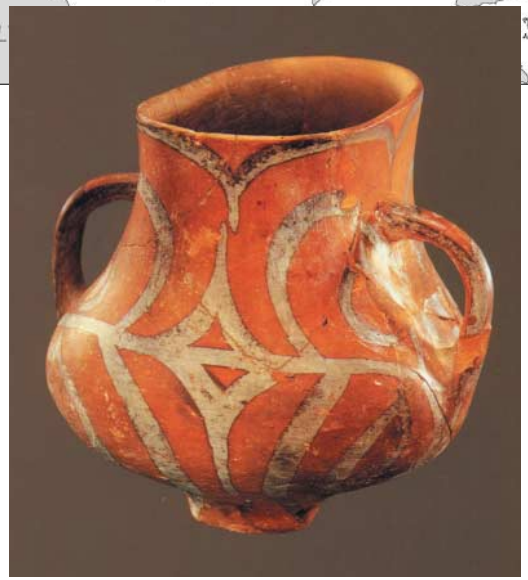
- Yes! If the sample can be placed in the beam as it is (es. metal coins)
  - Non-destructive
  - Bulk analysis

- No. Large samples (es. vases) → grind to powder a small part of the sample
  - Destructive
  - Punctual



Applications to Archaeology

- A group from the University of Oxford performed NAA on black-on-red Neolithic pottery (northern Greece)
- Insights into degree of standardization in the production and production scales
- They found different ceramic recipes within this specific ceramic group → this reflects variation in pottery traditions



V. KILIKOGLOU et al. University of Oxford, 2007, *Archaeometry* **49**, 2 (2007) 301–319

Applications to Archaeology

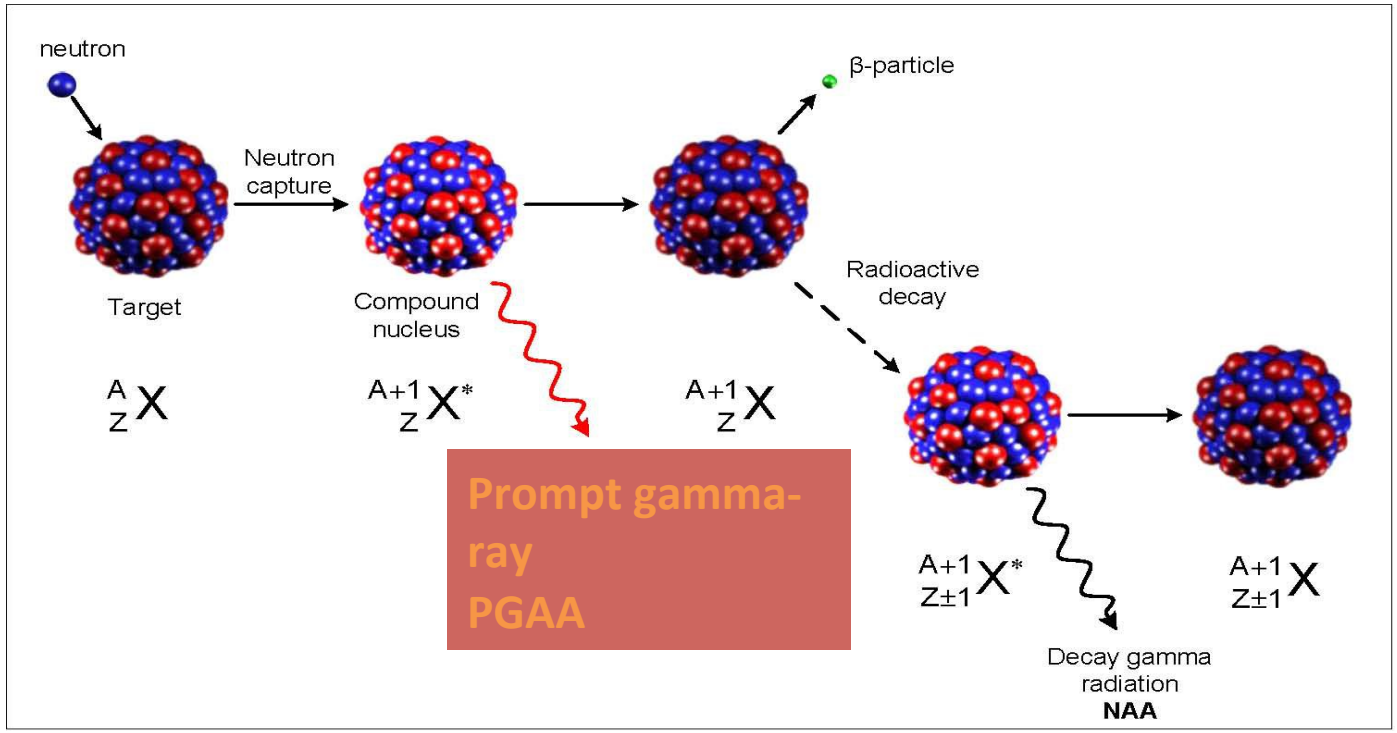
- D. Nichols and coworkers performed NAA studies on ceramic material from excavations at the site of Chiconautla, Mexico
- Insights into the relationship between markets, urbanism, and political development in the Basin of Mexico
- Better understanding of the ceramic exchange networks after the decline of the classic period

D. Nichols, C. M. Elson, L. G. Cecil, M. D. Glascock (America Museum of Natural History and University of Missouri Research Reactor)

Prompt Gamma Activation Analysis PGAA

PGAA Principle

- Uses the **prompt gamma rays** emitted **during neutron capture**, rather than the gamma rays emitted by the resulting radioisotope

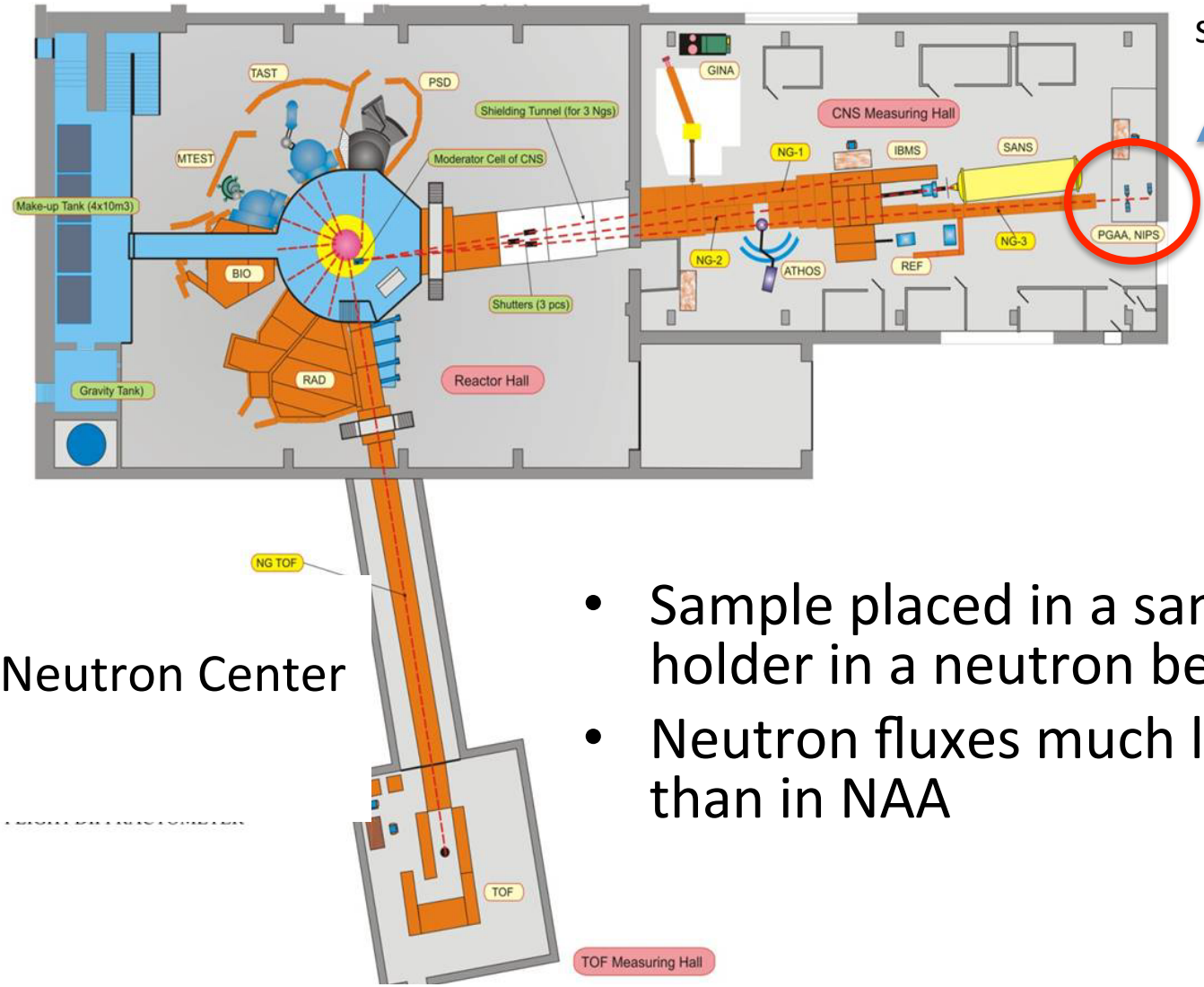


PGAA Principle

- PGAA is based on detection of capture gamma rays emitted by a target material while it is being irradiated with neutrons
- Nuclei formed in capture have excitation energies equal to the binding energy of the added neutron
- The excitation energy is released by emission of gamma rays of energies ranging from 100 keV to 10 MeV

PGAA Setup

PGAA Experimental station

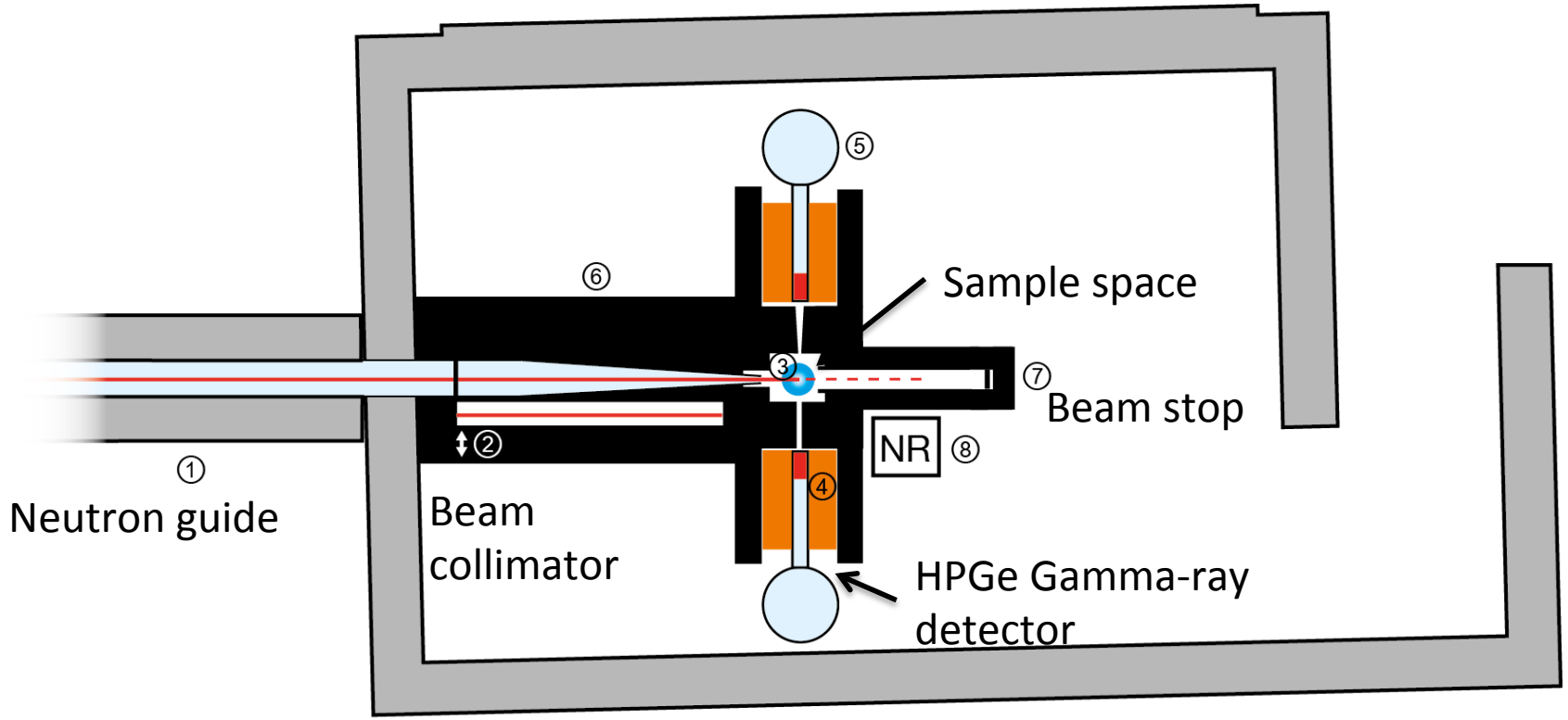


Budapest Neutron Center

- Sample placed in a sample holder in a neutron beamline
- Neutron fluxes much lower than in NAA

PGAA Setup

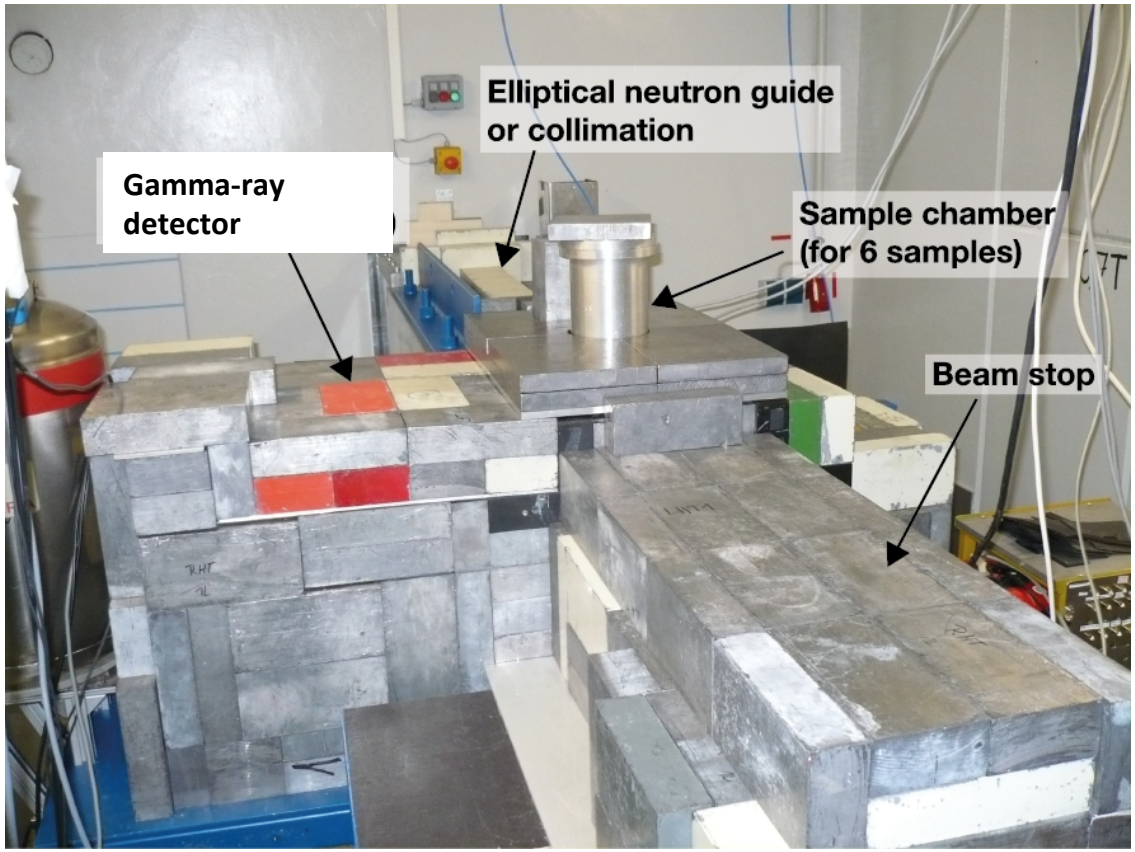
PGAA at Heinz Maier-Leibnitz Zentrum (Munich, Germany)



Taken from Heinz Maier-Leibnitz Zentrum

PGAA Setup

PGAA at Heinz Maier-Leibnitz Zentrum (Munich, Germany)



Taken from Heinz Maier-Leibnitz Zentrum

When to use PGAA

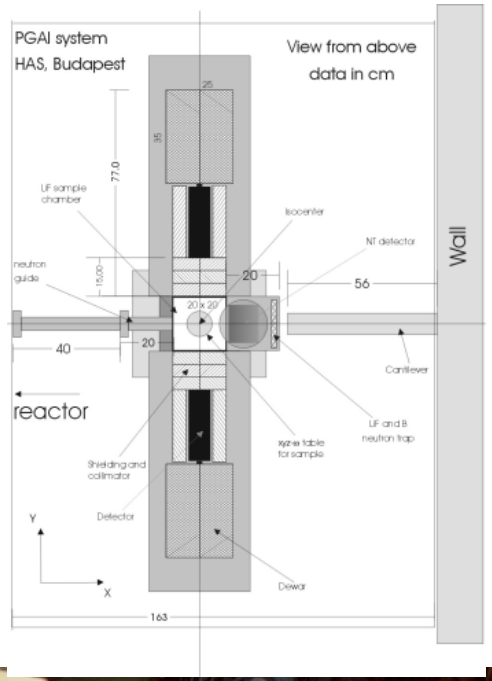
- The PGAA technique is most applicable to
  - elements with high neutron capture cross-sections (B, Cd, Gd)
  - elements which decay too rapidly to be measured by NAA
  - Elements producing only stable isotopes
  - elements with weak decay gamma-ray intensities
- 3D elemental composition of samples

PGAA and spatial information

- PGAA is a bulk elemental analysis → the measured concentrations represent the average composition of the irradiated part
- Spatial distribution of the elements by scanning the sample with a collimated neutron beam and using a collimated gamma-ray detector
- This method is called Prompt Gamma Activation Imaging

PGAI at the Budapest Research Reactor

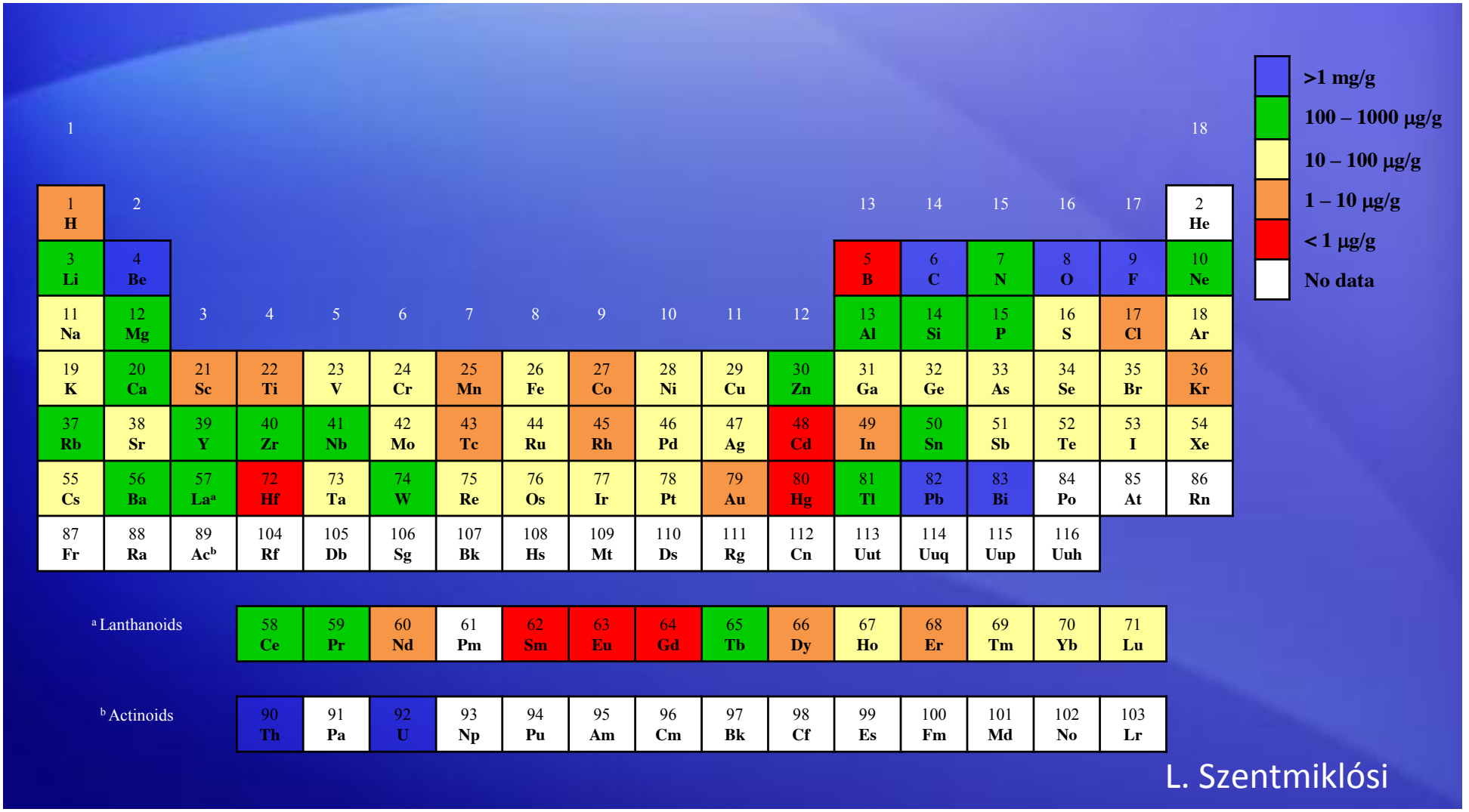
- Computer-controlled sample positioning table to measure hundreds of spectra from different positions in the sample
- Both neutron beam and gamma detectors highly collimated to achieve a spatial resolution of ~ 1 mm
- Massive lead shielding around the HPGe detector to improve the signal-to-background ratio
- Multiple detectors to shorten the needed beamtime



PGAA vs NAA

Technique	NAA	PGAA
# of peaks in the gamma-ray spectrum	10-100 peaks	1000-5000 peaks
Energy of gamma-ray radiation	100 keV – 3 MeV	100 keV – 12 MeV
Time required	> Weeks	Minutes/hours
Detection limit	Ppm-ppb	> ppm
Remaining activity	months	1-2 days

PGAA Detection limits



PGAA Applications to Archaeology

- Stone tools
- Ceramics
- Coins
- Pigments and painting
- Metal objects

Obsidian finds HNM

- Obsidian finds, Hungarian National Museum
- 11 obsidian cores analyzed at the PGAA station (Budapest Reactor Centre)
- Beam collimators and an adjustable sample stage used to analyze several parts of the samples
- Acquisition times: 1-1.5h

Zsolt Kasztovszky, Katalin T. Biró, Zoltán Kis, Journal of Lithic Studies (2014) vol.1

Obsidian finds HNM

Results→ Chemical composition. Concentration values for major components.

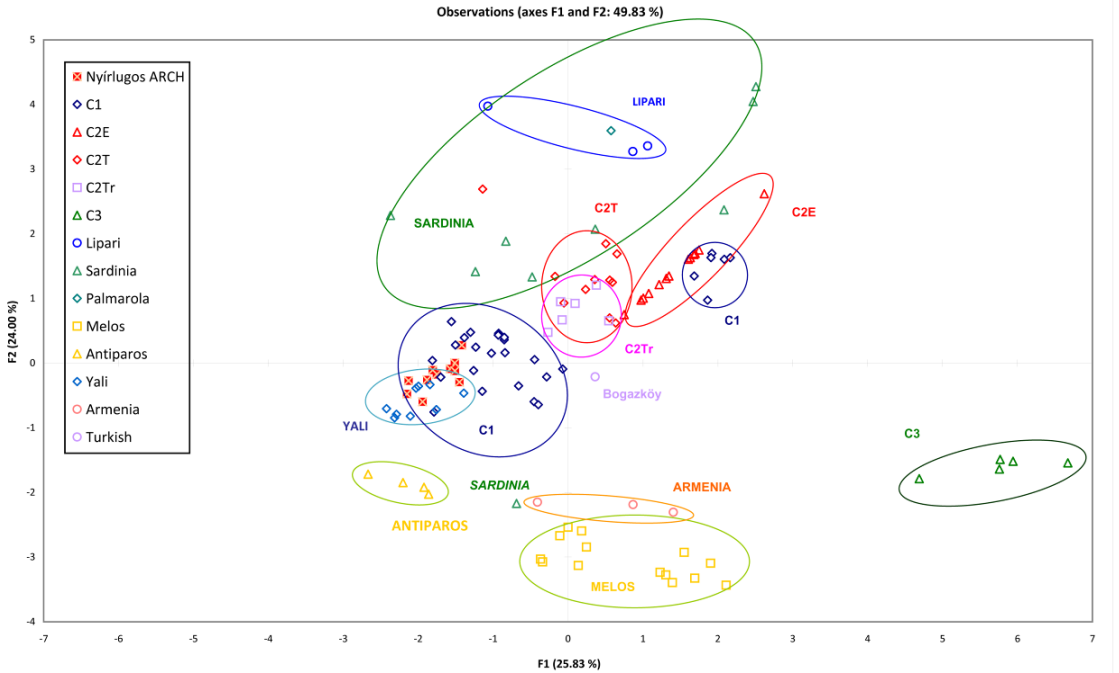
Inventory number (HNM)	SiO_2 (m%)	TiO_2 (m%)	Al_2O_3 (m%)	Fe_2O_3 (m%)	MnO (m%)	CaO (m%)	Na_2O (m%)	K_2O (m%)	H_2O (m%)	Cl (μg/g)	B (μg/g)	Sm (μg/g)	Gd (μg/g)	SUM (m%)
1923.28.01	76.5	0.044	12.7	1.06	0.049	0.79	4.11	4.55	0.13	484	38.5	3.26	3.73	99.99
1923.28.02	76.7	0.042	12.9	1.02	0.046	0.74	3.75	4.45	0.21	549	38.4	3.04	3.40	99.99
1923.28.03	77.2	0.043	12.6	0.96	0.054	0.75	3.55	4.56	0.15	518	38.9	2.83	3.53	99.99
1923.28.04	76.4	0.047	13.0	1.03	0.047	0.81	3.83	4.69	0.14	583	39.4	3.36	3.83	99.99
1923.28.05	76.6	0.048	12.9	1.05	0.051	0.85	3.82	4.48	0.17	563	38.5	3.21	3.31	99.99
1923.28.06	76.6	0.039	12.7	0.96	0.053	0.77	3.84	4.59	0.35	520	41.3	2.92	3.47	99.99

Zsolt Kasztovszky, Katalin T. Biró, Zoltán Kis, Journal of Lithic Studies (2014) vol.1

Obsidian finds HNM

- Provenance research
- Investigation of prehistoric trade

Separation of obsidian source regions



Zsolt Kasztovszky, Katalin T. Biró, Zoltán Kis, Journal of Lithic Studies (2014) vol.1

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- Michael D Glascock, Hector Neff, Meas. Sci. Technol.14 (2003) 1516–152]
- Concepts, Instrumentation and Techniques of Neutron Activation Analysis, Imaging and Radioanalytical Techniques in Interdisciplinary Research - Fundamentals and Cutting Edge Applications (2013)
- Leah Minc, Oregon State University Archaeometry Lab

Thank you