Trace Element Analysis of Geological, Biological & Environmental Materials By Neutron Activation Analysis: An Exposure

ILA PILLALAMARRI

Earth Atmospheric & Planetary Sciences
Neutron Activation Analysis Laboratory
Massachusetts Institute of Technology
Cambridge, MA 02139

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Session 5

- **12.091 Course – Students' individual presentations**
- **12.091 Assignment Review**
- **Neutron Activation Analysis –**

  Trace Element Geochemistry –

  Examples of applications

  Mineralogy

  Petrology

  Examples of studies done using MIT-EAPS INAA Laboratory
- **Conclusion –**

  Advantages of Neutron Activation Analysis

12.091 Course Student Presentations (see Projects section)

Wen-Fai Fong:

Delayed Neutron Activation Analysis

Martin D. Lyttle:

Epithermal Neutron Activation Analysis

Ian Garrick-Bethell:

Prompt Gamma Neutron Activation Analysis

Activity Equation Review

A = number of decays per second (Activity) dps

N = number of atoms of the target isotope

$$= \frac{m}{W} \times \theta \times 6.023 \times 10^{23}$$

m = mass of the element in the irradiated sample g

θ = isotopic abundance

w = Atomic weight of the element

λ = decay constant = $0.693/t_{1/2}$

$t_{1/2}$ = Half-life of the isotope

ϕ = neutron flux $n.cm^{-2}.sec^{-1}$

σ = activation cross-section $10^{-24}\ cm^2$

Activation Equation Review …

t_{irr} = irradiation time

$A = N \sigma \phi [1 - \exp(-\lambda t_{irr})]$

After a delay of time t_d

$A = N \sigma \phi [1 - \exp(-\lambda t_{irr})]\exp(-\lambda t_d)$

For a counting time of t_c

$A = N \sigma \phi [1 - \exp(-\lambda t_{irr})]\exp(-\lambda t_d) [1 - \exp(-\lambda t_c)]$

12.091 Assignment

1)In a house in Cambridge, the water from the faucet suddenly started showing some particulate matter, which is suspected to be copper from a pipe. It was brought to the MIT Reactor for analysis. You are asked to calculate the activity that would be produced by thermal neutron activation, if 1 gram of copper is irradiated in the reactor flux of 4×10^{12} $n.cm^{-2}.sec^{-1}$ for 2 hours.

i)On removal what is the activity of each copper isotope?

ii)What will be the activity of each isotope 1 hour after the removal from the reactor?

The answer should contain: the activity equation, the parameters and values used, and the activity calculated.

Suggested Use:

1) The Chart of Nuclide Handout,

2) Table of Nuclides Appendix D, p 606 -650,
   Gamma-ray sources Appendix E 651-660,
   Nuclear and Radiochemistry by
   G. Friedlander, J. Kennedy, E. S. Macias, J. M. Miller

Answer: The stable isotopes of copper are ^{63}Cu and ^{65}Cu.

Atomic weight of Cu = 63.546, flux = 4E12 $n/cm^2.sec$

^{63}Cu (n,γ) ^{64}Cu and ^{65}Cu (n,γ) ^{66}Cu are the thermal neutron activation reactions.

^{65}Cu (n,γ) ^{66}Cu:

$\sigma = 2.17E\text{-}24\ cm^2$, $\theta = 30.83\%$, ^{66}Cu half life = 5.10 m,

The activity of ^{66}Cu upon removal = 0.69 curies and after 1 hour 0.197 mCi

^{63}Cu (n,γ) ^{64}Cu:

$\sigma = 4.4E\text{-}24\ cm^2$, $\theta = 69.17\%$, ^{64}Cu half life = 12.75 h,

The activity of ^{66}Cu upon removal = 0.321 curies and after 1 hour 0.304 mCi

12.091 Assignment

2)An entrepreneur wants to know whether a particular area of interest has Molybdenum and Antimony. So what are the radioisotopes that can be used for the thermal neutron activation analysis.

Provide all the relevant information of the X (n,γ)Y reaction, identify the parent and daughter nuclei, the activation cross section, the half-life of the daughter product, and the predominant gamma-ray energy for identification.

Suggested Use:

Table of Nuclides Appendix D, p 606 -650,

Gamma-ray sources Appendix E 651-660,

Nuclear and Radiochemistry by

G. Friedlander, J. Kennedy, E. S. Macias, J. M. Miller

Answer:

The stable isotopes of Molybdenum are ^{92}Mo, ^{94}Mo through ^{98}Mo, and ^{100}Mo.

The thermal neutron activation reactions are:

^{92}Mo (n,γ) ^{93}Mo, $\sigma = 0.006E\text{-}24\ cm^2$, $\theta = 14.8\%$, ^{93m}Mo half life = 6.9 h

^{98}Mo (n,γ) ^{99}Mo, $\sigma = 0.131E\text{-}24\ cm^2$, $\theta = 24.13\%$, ^{99}Mo half life = 65.94 h

^{100}Mo (n,γ) ^{101}Mo, $\sigma = 0.200E\text{-}24\ cm^2$, $\theta = 9.63\%$, ^{101}Mo half life = 14.6 m

^{98}Mo (n,γ) ^{99}Mo can be selected and the identifying gamma-ray energy is 739.4 keV

12.091 Assignment

Answer 2 continued.

The stable isotopes of Antimony are ^{121}Sb and ^{123}Sb

The thermal neutron activation reactions are:

^{121}Sb (n,γ) ^{122}Sb, σ = 6.33E-24 cm^2 , θ = 57.3%, ^{122}Sb half-life = 2.72 d

^{121}Sb (n,γ) ^{122m}Sb, σ = 0.05E-24 cm^2 , θ = 57.3%, ^{122m}Sb half-life = 4.21 m

^{123}Sb (n,γ) ^{124}Sb, σ = 4.08E-24 cm^2 , θ = 42.7%, ^{124}Sb half-life = 60.2 d

^{123}Sb (n,γ) ^{124m}Sb, σ = 0.03E-24 cm^2 , θ = 42.7%, ^{124m}Sb half-life = 93 s

^{121}Sb (n,γ) ^{122}Sb can be chosen for short irradiation time, the identifying gamma-ray energy is 564 keV.

^{123}Sb (n,γ) ^{124}Sb can be chosen for longer irradiation time, the identifying gamma-ray energy is 603 keV.

Note: The meta stable isotopes are short lived.

12.091 Assignment

3)An unknown sample powder was found in an envelope. It was brought to the reactor for analysis.

The gamma spectrum revealed significant gamma-ray peaks of energy 320 KeV, 1368 keV and 2754 keV. Identify the content of the powder.

Suggested use:

Appendix 5, Table 2

Neutron Activation Analysis

By D. De Soete, R. Gijbels, J. Hoste

Answer:

$^{50}Cr\ (n,\gamma)\ ^{51}Cr$; 320 kev gamma-ray is emitted by ^{51}Cr

$^{23}Na\ (n,\gamma)\ ^{24}Na$;

1368 kev and 2754 keV gamma-rays are emitted by ^{24}Na.

So the powder contains Sodium and Chromium.

12.091 Assignment

4)The weights of empty vial, empty vial + sample powder were taken 6 times . Write the formula for the propagation of errors, calculate the error in the weight of the sample powder. Interpret the results.

Weights (in grams) of the empty vial, weighed separately for 6 times:
1.14470, 1.14475,1.14472, 1.14476, 1.14478, 1.14475
Weights (in grams) of the vial + sample powder, weighed separately for 6 times:
1.35041, 1.35040, 1.35029, 1.35018, 1.35026, 1.35035

Answer:
Weights (in grams) of the empty vial, weighed separately for 6 times:
1.14470, 1.14475,1.14472, 1.14476, 1.14478, 1.14475
Average weight = 1.14474
Standard Deviation = 0.000026
Precision = 0.2%

Weights (in grams) of the vial + sample powder, weighed separately for 6 times:
1.35041, 1.35040, 1.35029, 1.35018, 1.35026, 1.35035
Average weight = 1.35037
Standard Deviation = 0.0000822
Precision = 0.6%

Propagated error = sqrt ($((0.000026)^2 + (0.0000822)^2)$
Sample weight = 0.20557 $\pm$ 0.0000862
Error in sample weight = 4%

The sample weight error is 4% due to losing the water into air, during weighing that day.

12.091 Assignment

5) Arsenic is determined in river sediment samples.
The abundance of As in the standard is 145 ppm.
The gamma-ray energy of ^{76}As is 559 keV.
The gamma peak areas of the sample and standard are respectively,
32699, and 1533496 for the same counting times.
The delays from the end of irradiation for the sample and the standard counting are 5.953 d, and 4.252 d.
The weights of the sample and standard are 0.38476 g and 0.41669 g.
Calculate the abundance in the sample.
Estimate the propagation of errors. You may use the weighing error from problem 4 above.
Answer:
^{76}As half-life is 26.32 h

	Standard	Sample	
Areas	1533496	32699	
Delay	4.252 d	5.953 d	
Areas	22529824	1407650	(Areas corrected to the end of irradiation)
Mass	0.41699	0.38476	
Abundance	145 ppm	??	

Abundance = 145 x [(1407650/0.38476) /(22529824/0.41699)] = 9.81 ppm
Standard deviation of peak area of standard = sqrt(1533496) = 1238
Standard deviation of peak area of sample = sqrt(32699) = 181
Error in sample weighing = 4%
Error in Abundance = sqrt(9.81^2 x [$(1238/1533496)^2$ + $(181/32699)^2$ + $(0.02/0.41699)^2$ + $(0.02/0.38476)^2$] = 0.69

The abundance in the sample is 9.81 ± 0.69 ppm or 9.8 ± 0.7 ppm or 10 ± 1 ppm.
So the error in the abundance determination is 10%, the main error coming from the weighing.

12.091 Assignment

6)In the EAPS INAA Laboratory, an internal standard has been analyzed 10 times. Nd is one of the Rare Earth Elements. Its measured abundance values (in ppm) are

24.0 ± 0.7, 23.7 ± 0.7, 24.0 ± 0.5, 24.3 ± 0.9, 23.7 ± 1.0,

24.3 ± 1.0, 24.0 ± 0.7, 23.8 ± 0.6, 24.0 ± 0.7, 24.7 ± 0.9.

The reference value of this standard is 24.7 ± 0.3.

Write the formulae and calculate the precision and accuracy of this measurement. Express the precision and accuracy in percentage.

Average value of Nd = 24.05

Standard Deviation = 0.31

Precision of the Nd measurement = 1.28% (Note: This is a simplistic version)

Accuracy = modulus(24.05-24.7) *100/24.7 = 2.63%

12.091 Assignment

7)Our department chairperson came to know that an equipment grant would be available soon. So a memo was sent to our gamma-spectroscopy group asking the importance of gamma spectrometer.

Write the usefulness of a gamma spectrometer.

Describe the components of a gamma spectrometer.

Look at the latest products. To look at the website http:// www.canberra.com and look under product category and do a write up - one or two lines of each product you want to select

Answer: Not provided

12.091 Assignment

8)The Department of Agriculture came to know that some fruit trees in Florida got contaminated. So they want to send some dry leaves for analysis of arsenic. Suggest a suitable standard.

Suggested use:
http://www.nist.gov

NIST Products and Services

Using the online Catalog (click on)

Advanced Search (click on)

Enter Keyword
(suggested keywords: agriculture, leaves)

View Certificate of Report and note down the information

Suggest your choice of the standard.

Answer: Not provided

12.091 Assignment

9)The MIT Libraries has asked you for some suggestions for new books on neutron activation analysis. What book titles can you suggest, which they do not already own?
Suggestions:
http://libraries.mit.edu/vera
type Books in Print in the search box
the next window opens
type keyword in the Quick search box.
Suggested keywords:
Neutron activation analysis
Nuclear analytical
Environmental geochemistry ...
Any keyword of your interest or field
You may search the Title in the Barton Search box to see whether that book already exists in the MIT library.
Barton, the Libraries online catalog.

12.091 Assignment

Answer 9:

1)The Atomic Finger Print: Neutron Activation Analysis,
B. Keisch, University Press of the Pacific, 2003.
2) Radioanalytical Methods in Interdisciplinary Research: Fundamentals in Cutting Edge Applications,
C. A. Laue and K. L. Nash , Oxford University Press, 2003.
3) Nuclear Analytical Techniques in Archaeological Investigations Technical Report Series 416,
International Atomic Energy Agency, 2003.
4)Activation Analysis in Environmental Protection,
V. M. Nazarov and M. V. Frontasieva, Hadronic Press, 1995.
5) The Physics of Big Sample Instrumental Neutron Activation Analysis,
R. M. Overwater, Delft University Press, 1994.
6)Nuclear Analytical Methods in Life Sciences,
J. Kucera, I. Obrusnik and E Sabbioni, Humana Press, 1994.
7)Nuclear Techniques for Analytical and Industrial Applications
G. Vourvopoulos and T. Paradellis, World Scientific Company 1993

12.091 Assignment

10)Now that you are familiar with trace element analysis of materials by neutron activation analysis, briefly describe its application by giving one example.

Answer: Not provided

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Applications of Neutron Activation Analysis in Geological Sciences

1)Trace impurities in diamonds: By determining the trace impurities, the inclusions of the parental melt from which the diamonds crystallized were studied.

2)Trace element analysis of Minerals:

A variety minerals like apatite, calcite, feldspar, galena, garnet, monazite, tourmaline are analyzed for trace elements, to determine element partitioning between phenocryst phase and coexisting matrix.

3)Trace Multi-element analysis of bulk rocks:

Trace multi-element analysis on wide variety of terrestrial, lunar, meteoritic materials were analyzed to determine the origin of fragments.

Applications of Neutron Activation Analysis in Geological Sciences…

4)**Rare Earth Element (REE) Analysis**: Neutron Activation Analysis is especially useful in determining the REEs and in the development of Trace Element Geochemistry of wide variety of rocks and minerals to understand the affect of petrogenetic processes on REE abundances. From the REE analyses, partition coefficients are determined to understand the fractionation and melting process. REE abundances normalized to chondritic values also provide information about spatial variation.

The comparison of chondrite normalized REEs of terrestrial basalts and the lunar rocks provided the first information of negative Eu anamolies in the lunar rocks which indicated the importance of feldspar in the early evolution of the moon.

Applications of Neutron Activation Analysis in Geological Sciences …

5)MIT-EAPS Prof. Fred Frey group has been involved in trace element geochemical work using instrumental neutron activation analysis, performing work under Ocean Drilling Project (ODP), Deep Sea Drilling Project (DSDP), Hawaii Scientific Drilling Project (HSDP) to study Mid Ocean Ridge Basalts (MORBs), Ninetyeast Indian Ridge, Kerguelen Plateau (Plume and Mantle), Lavas from Hawaiian Islands (Haleakala, Kahaoolawe, Kilauea, Koolau, Mauna Kea), Lavas from Andean volcanoes of Chile, Lavas from volcanoes of Iceland.

Reference:

MIT_EAPS Activation Analysis and Radiometric Laboratory Contribution to Geoscience: Past, Present and Future, (Poster)

P. ILA (Ila Pillalamarri)

Low Radioactivity Techniques LRT2004, Laurentian University, Sudbury, Canada, December 12-13, 2004

http://lrt2004.snolab.ca

Conclusion

Neutron Activation Analysis:

Several important advantages over other techniques like Atomic Absorption, X-Ray Resonance Fluorescence, Inductively Coupled Plasma Atomic Emission Spectrometry, Inductively Couples Plasma Mass Spectrometry:

1. **Nuclear technique that measures the intensity of gamma rays of " characteristic" energy using gamma spectroscopy.**
2. **Multielement Analysis.**
3. **Rapid analyses of multiple samples.**
4. **Sample size can be variable (typically 1 mg to 1 gm).**

Applications of Neutron Activation Analysis in Geological Sciences…

6)Analysis of Reference Standards:

Neutron Activation Analysis is very useful for analysis of materials for the purpose of preparing the reference standards.

MIT-EAPS INAA has participated regularly in the analysis of reference standards.

Reference:

Trace element concentrations of new USGS standards AGV2, BCR2, BHVO2, DTS2 and GSP2 by instrumental neutron activation analysis, P. Ila and F. A. Frey,
Modern Trends in Activation Analysis, MTAA10, Bethesda, MD, U. S. A., April 19-23, 1999
Journal of Radioanalytical and Nuclear Chemistry 244 (2000) 599-602.

Conclusion …

5. Nondestructive - that is valuable and safe, samples are not destroyed.

6. No Chemical processing; therefore samples are not contaminated during sample preparation, no uncertainty about total dissolution of sample, no need for dilutions of solutions, making the technique valuable and safe. Samples are not destroyed.

7. No need for repeated blank measurements because no memory effects.

8. Gamma ray spectroscopy is largely free from matrix interferences

9. Depending on the sample matrix, elemental concentrations can be determined at parts per million (ppm), parts per billion (ppb) and parts per trillion (ppt) level.

10. Versatile (in use for more than half a century), well established and reliable.

References

1. Trace element geochemistry – Applications to the igneous petrogenesis of terrestrial rocks
F. A. Frey
Rev. Geophys. Space Phys. 17(4) (1979) 803-823.
2. Ring of Fire
http://pubs.usgs.gov/publications/text/fire.html
3.Plate tectonics from the US Geological Service
http://pubs.usgs.gov/publications/text/historical.html#anchor4833509
4.Mid Ocean Ridge Basalts (MORB)
http://www.agu.org/revgeophys/kinzle01/node3.html
5. Continental Drift
http://pubs.usgs.gov/publications/text/developing.html
6.Hawaii Scientific Drilling Project Press Release
http://expet.gps.caltech.edu/press.html
7.Ninetyeast Indian Ridge – Kerguelen Plateau
http://www.ga.gov.au/odp/publications/183_SR/005/005_f1.html
(Frey et al 2000)
8.Trace element concentrations of new USGS standards AGV2, BCR2, BHVO2, DTS2 and GSP2 by instrumental neutron activation analysis
P. Ila and F. A. Frey,
Modern Trends in Activation Analysis, MTAA10, Bethesda, MD, U. S. A., April 19-23, 1999
Journal of Radioanalytical and Nuclear Chemistry 244 (2000) 599-602.

9.MIT_EAPS Activation Analysis and Radiometric Laboratory Contribution to Geoscience: Past, Present and Future, (Poster)
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12.091 Session 5 End

12.091 Course End