Fracking Fluids & Radioactivity

ACZ Laboratories, Inc.

A Full Service Environmental Testing Laboratory

Outline & Agenda

- Who Am I – Background, Interests, etc.
- ACZ Laboratories – this is my Plug!
- Subject Topic – Matrix Interferences
- Conclusions – Possible Solutions
- Questions – Ask Anytime

ACZ Laboratories

Matrix Complications

Radioactive content of produced fluids and flowback wastewater

- Naturally-Occurring Radioactive Materials (NORM)
  - Elevated concentrations of radium (Ra) isotopes, Ra-226 & Ra-228
- The "Marcellus Shale" Paper
  - Nelson, A. W., *et al*, Matrix Complications in the Determination of Radium Levels in Hydraulic Fracturing Flowback Water from Marcellus Shale, *Environmental Science and Technology Letters* 2014, *1*, 204—208
- Client Concern Regarding Radioactivity & Environmental Impact
  - Accurate assessment of the radioactivity

Fundamentals of Radiation

Radiation is the emission of high energy particles and/or electromagnetic waves

- ✓ Energy in motion

Radioactivity is the spontaneous emission of radiation from the nucleus of an unstable atom

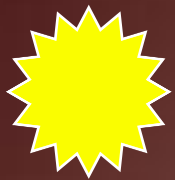
Isotope is an atom with the same number of protons, but different number of neutrons (*i.e.*, different forms of a given element)

Radioisotope is an unstable isotope of an element that decay or disintegrates spontaneously, emitting radiation

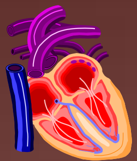
- ✓ Approximately 5,000 natural & artificial radioisotopes have been identified

Radioactive Sources

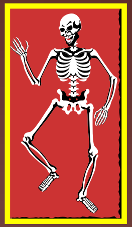
Solar Radiation



Nuclear Medicine



X-Rays



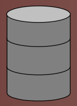
Cosmic Rays

Consumer Products

Elements

Food & Drink

Radioactive Waste



Terrestrial Radiation

Nuclear Power

Each Other

Terrestrial Radiation

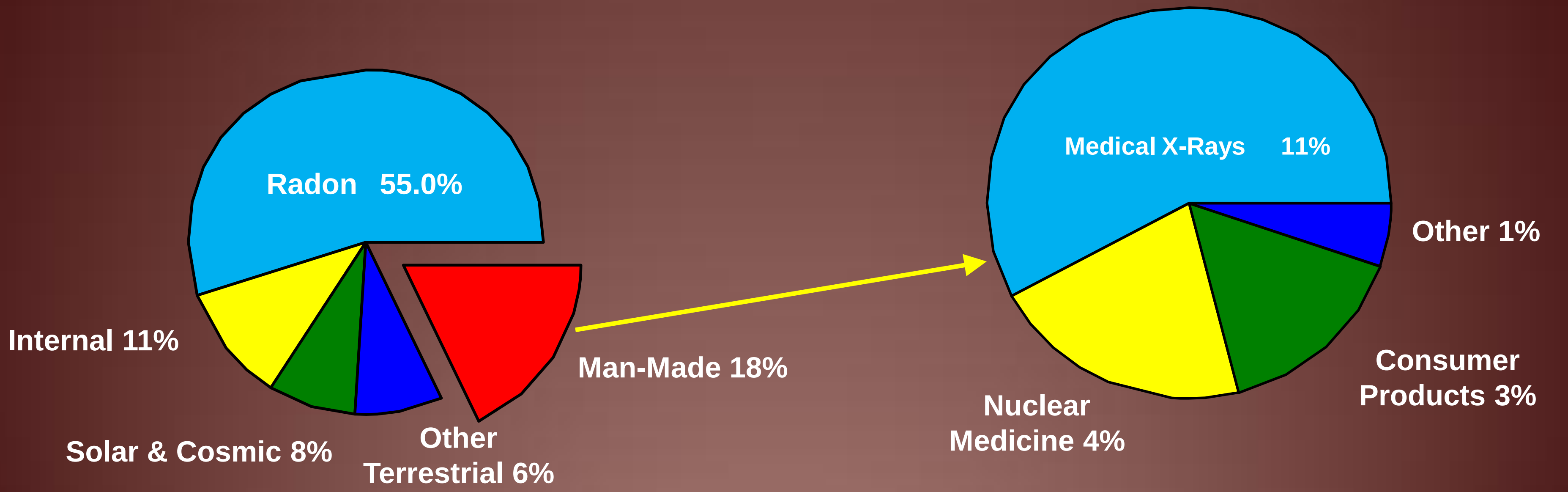
The most important radionuclides that enter the body are terrestrial in origin

- Greatest contributor is Ra-226 (Radium) with significant levels also from U-238, Th-232, and K-40
  - Igneous rock contains the highest concentrations
  - Fly ash from coal burning plants contains more radiation than that of nuclear or oil-fired plants
- Enters the body through the food we eat, water we drinks, and the air we breathe
- Used and eliminated during normal metabolic mechanisms

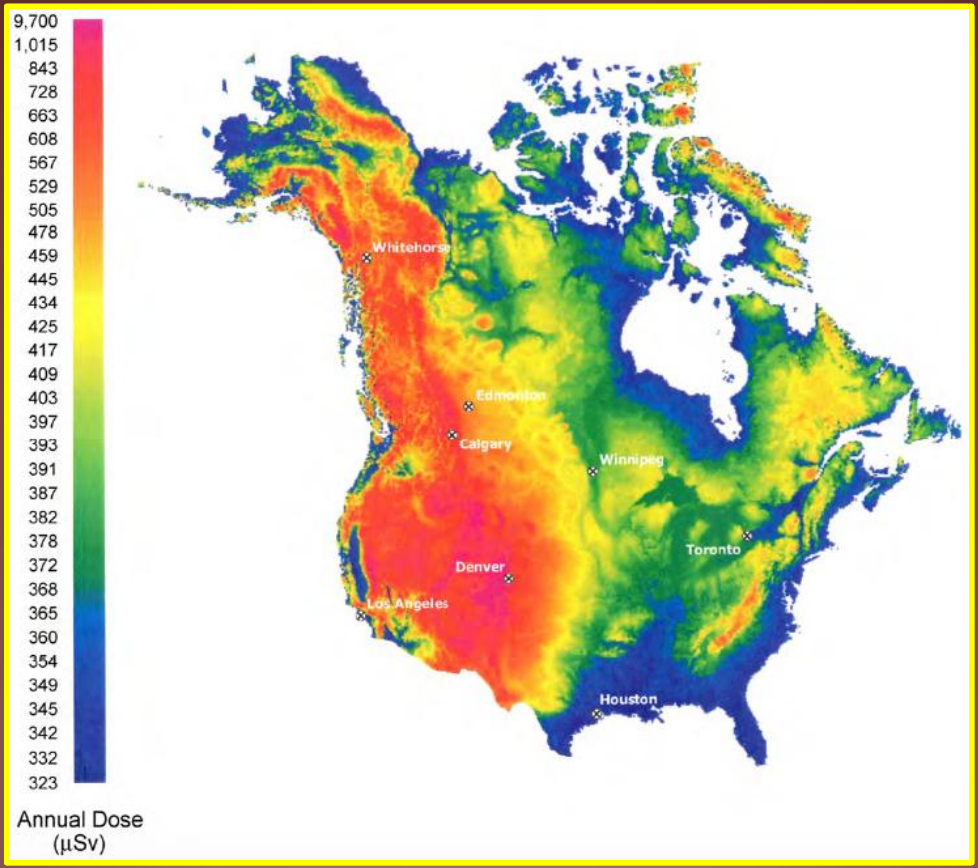
Annual Dose from Background Radiation

Total exposure

Man-made sources



Map of Annual Doses in North America



- Grasty and LaMarre, 2004; Figure 3.4 from NCRP 160 (http:// NCRPonline.org)

Regulatory Compliance & Information

Health Concerns → avoid quantities of radionuclides ending up in waste water treatment plants which ends up in the drinking water

- Most drinking-water sources have very low levels of radionuclides
  - Radium-226, Radium-228, & Uranium
- Typically, limits are less than the limits set by the United States Environmental Protection Agency (EPA)

Exasperating a Problem

Response to Flowback/Produce Water

Results in a quickened and/ or incautious response often resulting in:

- The lack of data quality objectives, and
- Consideration regarding the issue when (or if) current method criteria fails
    - Methods 903.0/903.1 and 904 for Radium-228 & Radium-226 detection

It is important to develop and validate effective methods for analysis of radionuclides in flowback/produce ware (PB/PW) because they are critical to appropriate regulatory, safety, and business decisions.

Response to Flowback/Produce Water

EPA methods are susceptible to matrix issues

- High total dissolved solids creates substantial competition in precipitation & coprecipitation separations
  - Individual elements (such as Ca, Sr, Ba, Group II alkaline earth metals) present in elevated amounts directly interfere with the chemistry
  - High solids content exceeds some of the method-specific limits
- Biphasic (or multi-layer) samples

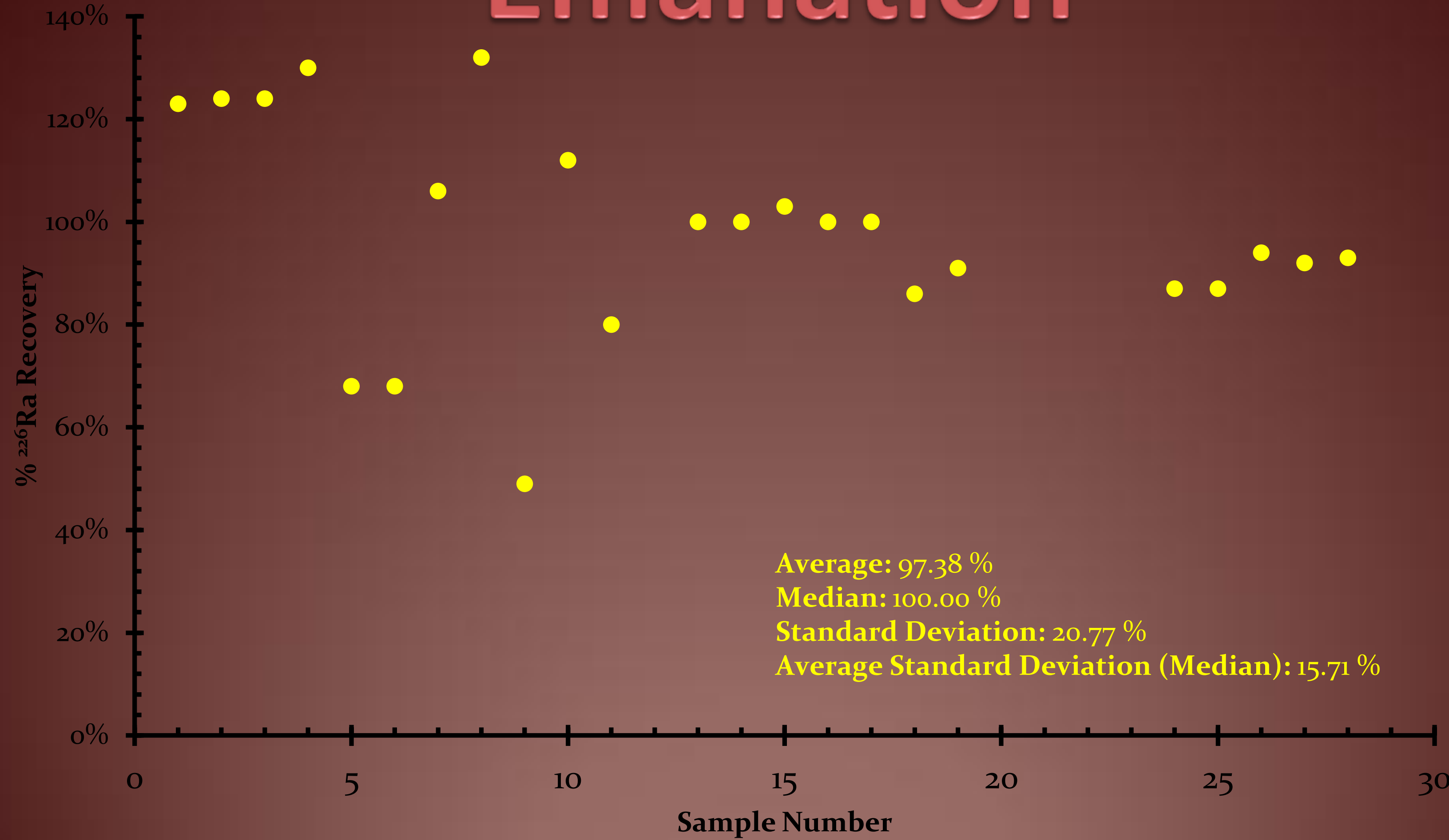
Post-Matrix Modification

Barium Sulfate ($BaSO_4$) Recovery

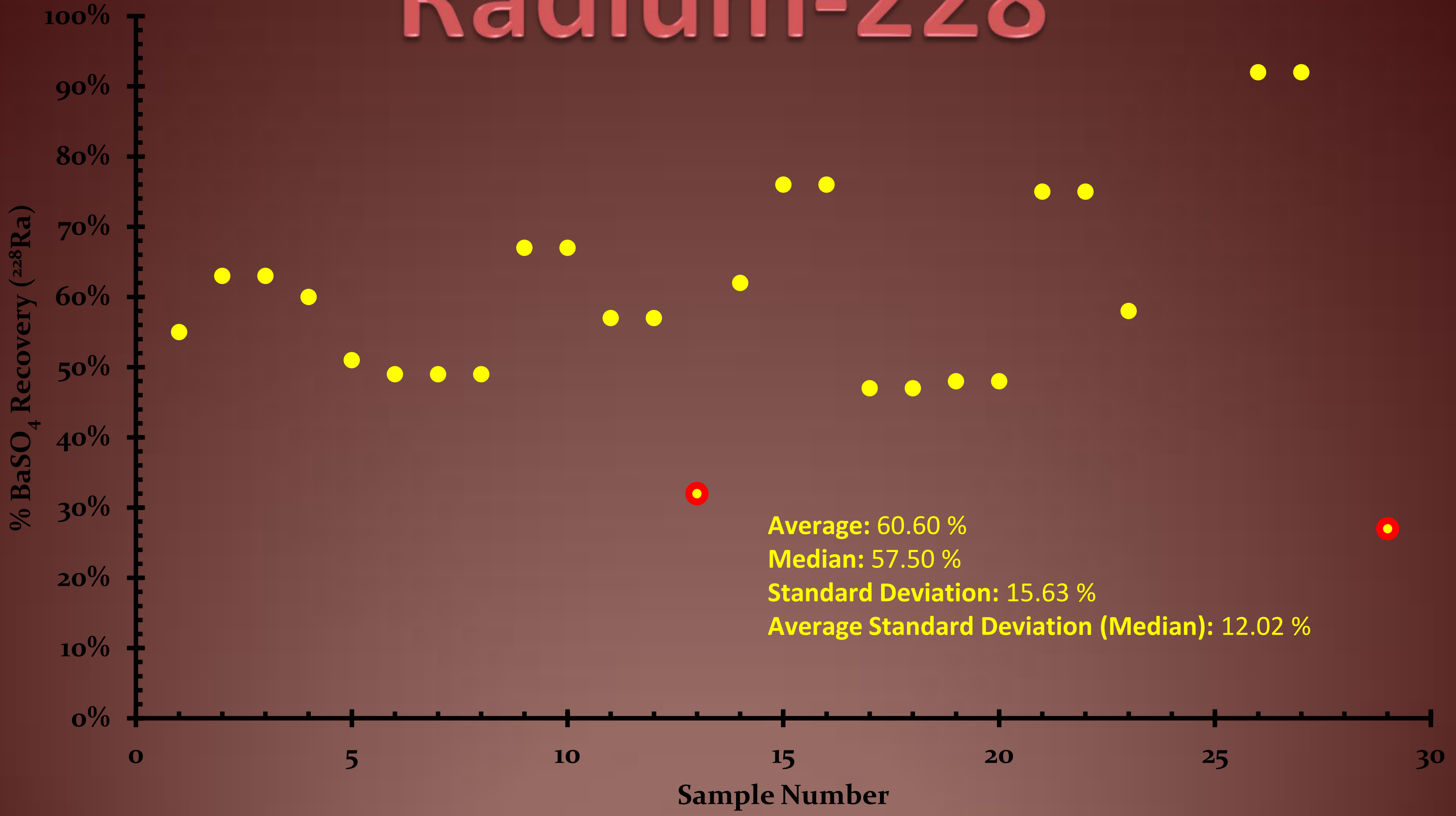
Coprecipitation Recovery

Biphasic Matrix

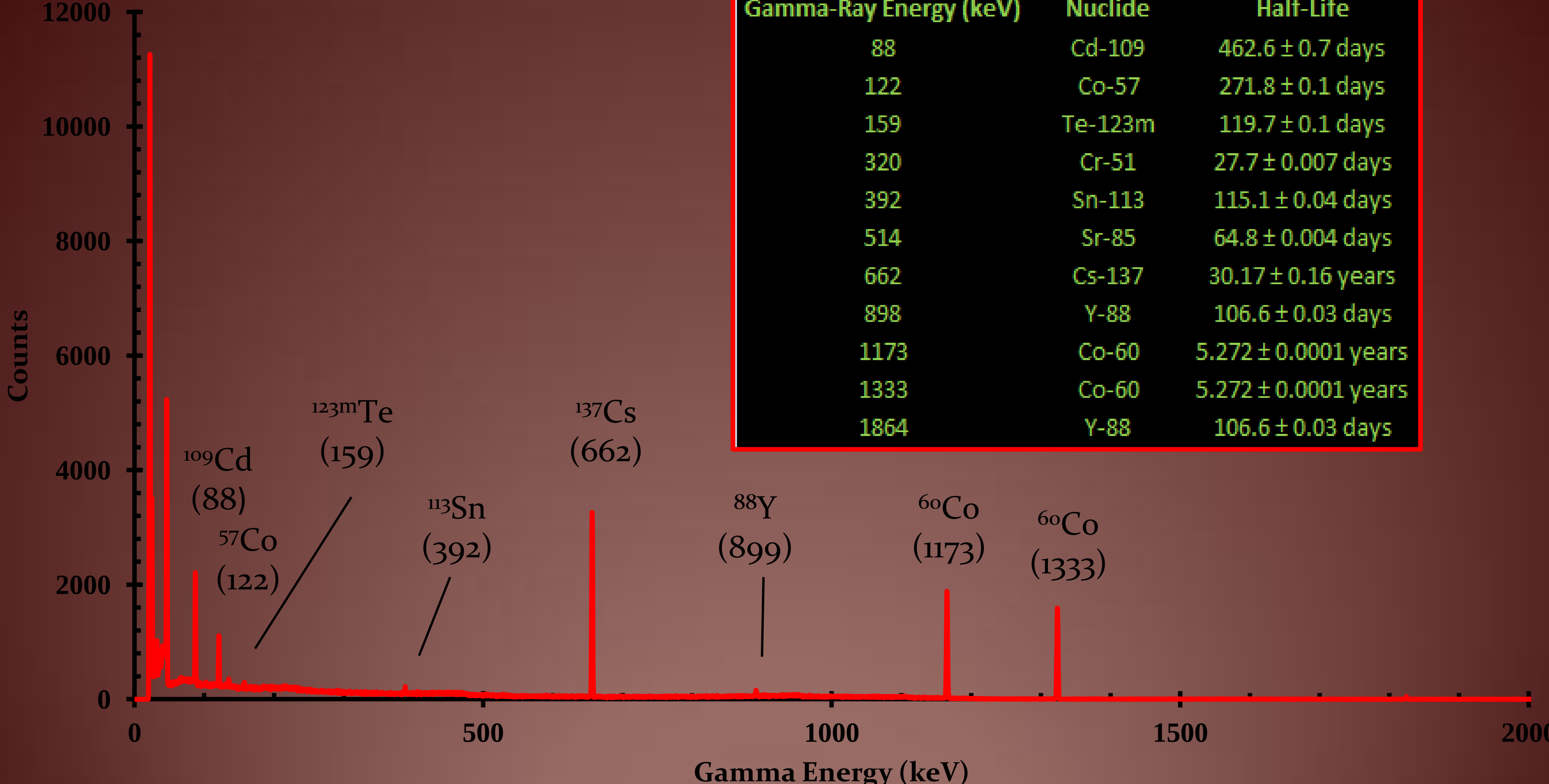
Method 903.1 – Radon Emanation



Method 904.0
Radium-228

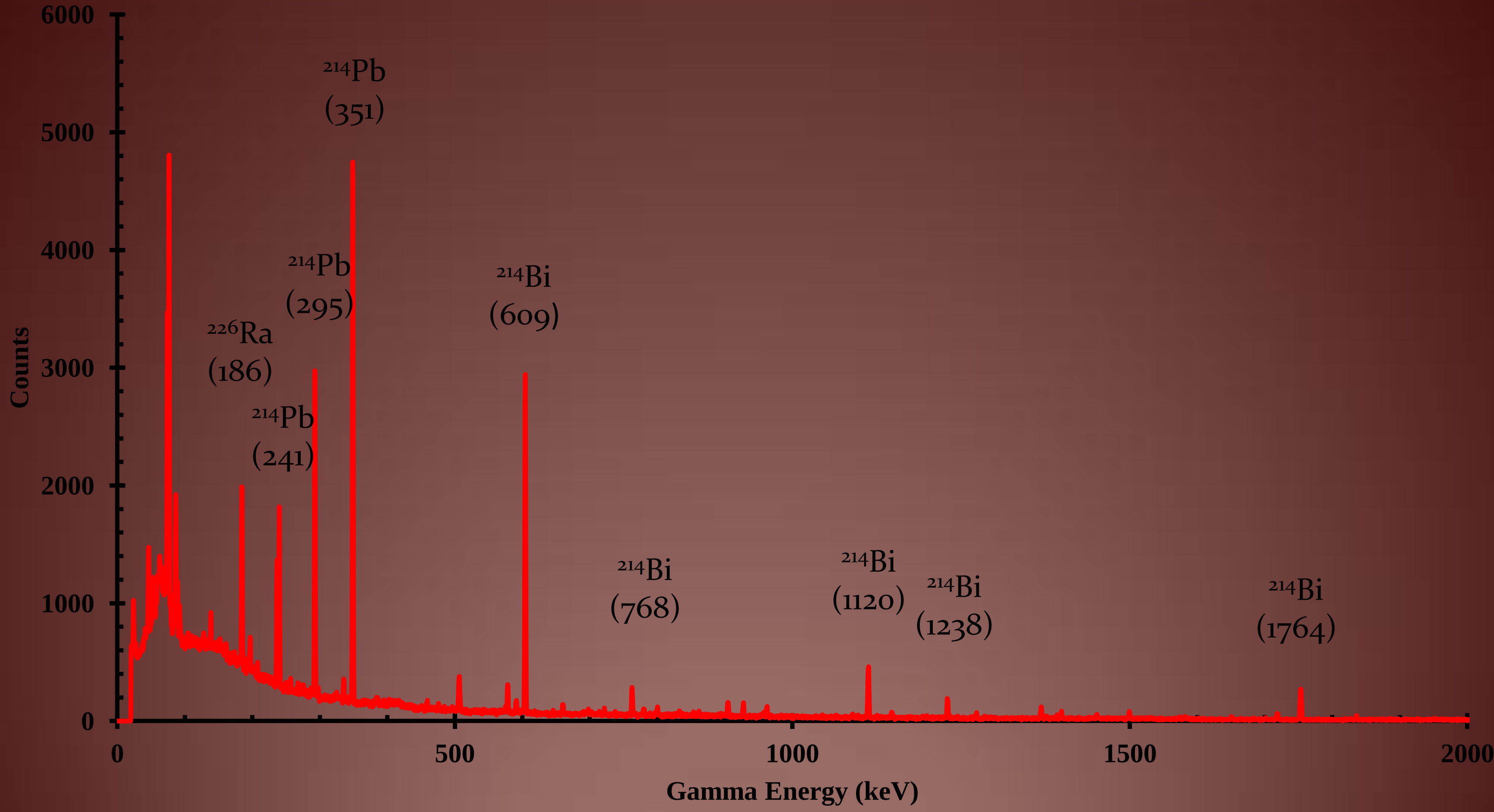


Gamma Spectroscopy

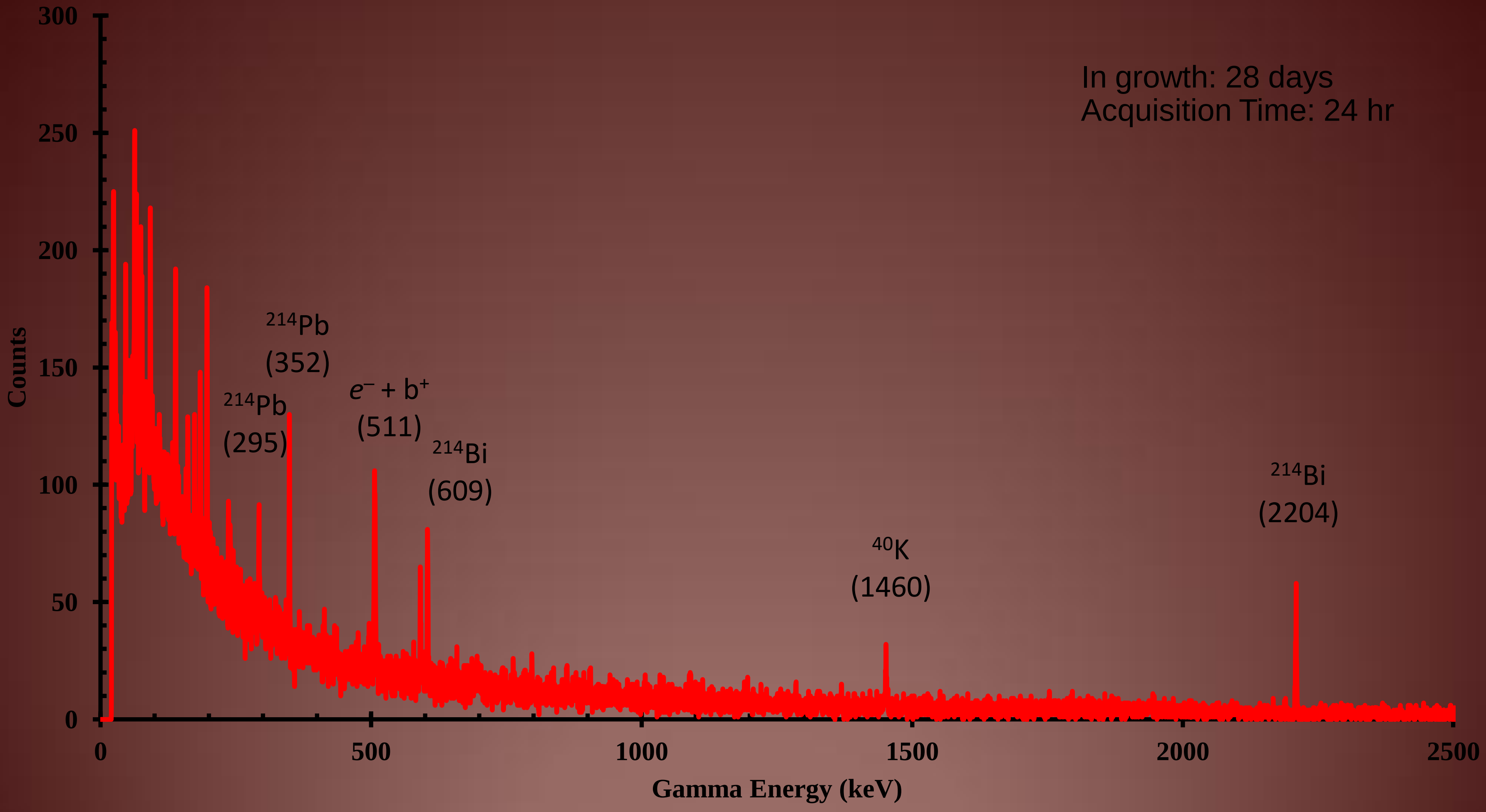


Gamma-Ray Energy (keV)	Nuclide	Half-Life
88	Cd-109	462.6 ± 0.7 days
122	Co-57	271.8 ± 0.1 days
159	Te-123m	119.7 ± 0.1 days
320	Cr-51	27.7 ± 0.007 days
392	Sn-113	115.1 ± 0.04 days
514	Sr-85	64.8 ± 0.004 days
662	Cs-137	30.17 ± 0.16 years
898	Y-88	106.6 ± 0.03 days
1173	Co-60	5.272 ± 0.0001 years
1333	Co-60	5.272 ± 0.0001 years
1864	Y-88	106.6 ± 0.03 days

Radon-226 Standard

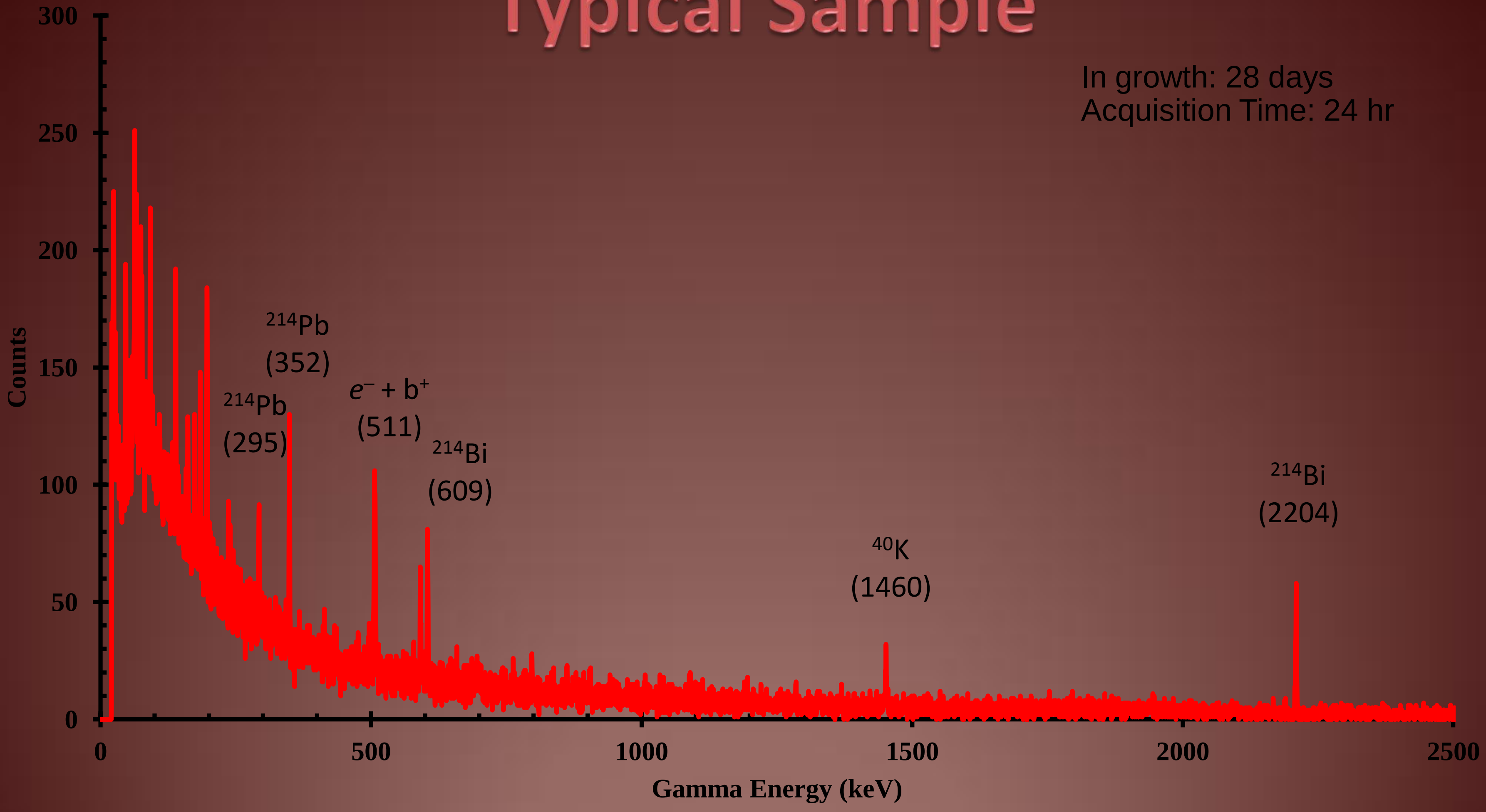


Gamma Spectrum Sample



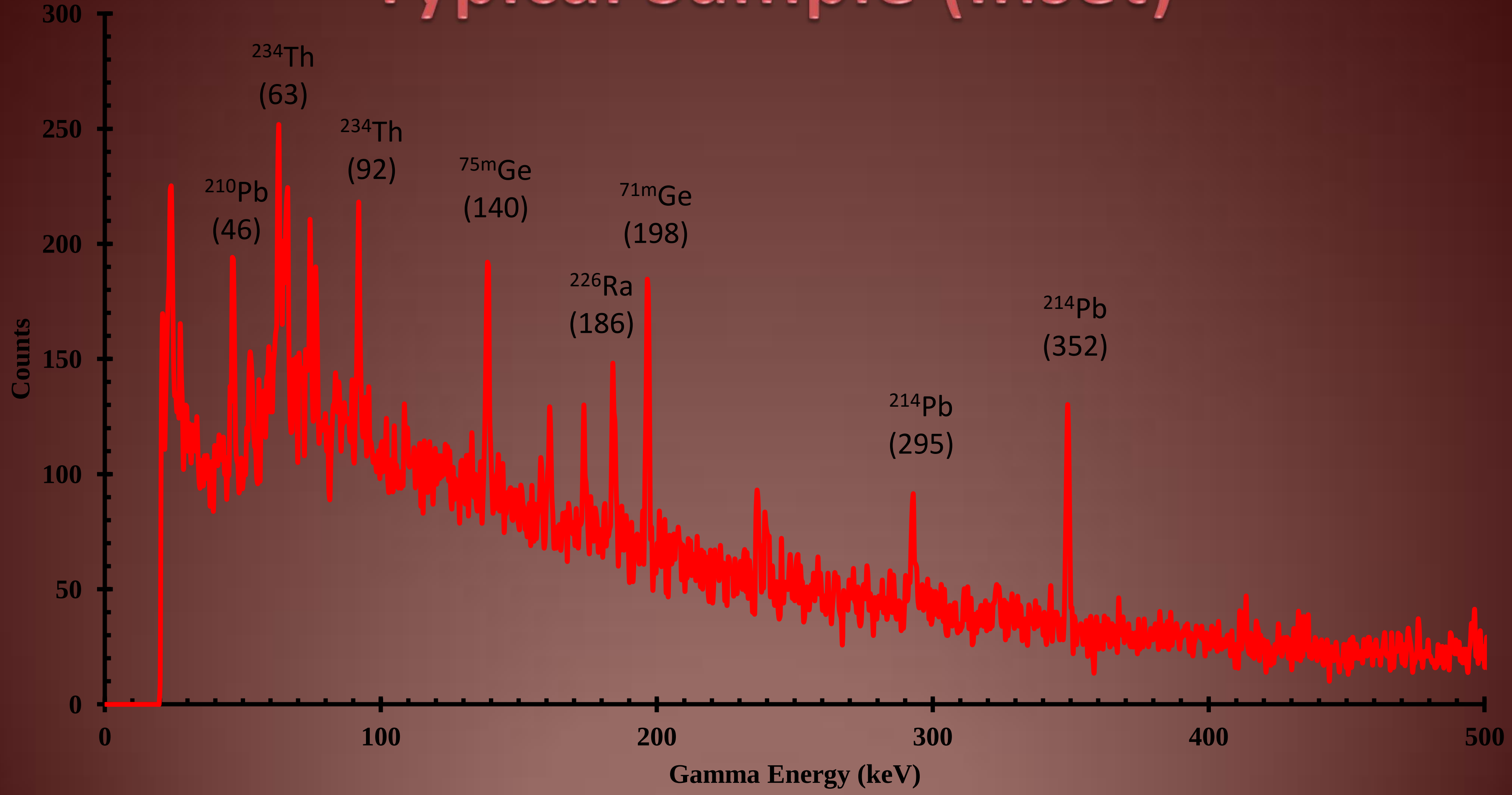
Gamma Spectrum

Typical Sample



Gamma Spectrum

Typical Sample (Inset)



Estimation of Ra-228 Concentrations

Ra-226 609.1 keV 94% ± 23

Ra-226 STANDARD
@ 20.0 pCi/L

↓

γ-SPECTROSCOPY
23.4 pCi/L

TEST SAMPLE
210 pCi/L via 903.1

↓

γ-SPECTROSCOPY
149.1 pCi/L

$$A_S = \left[\frac{1}{V \times D_S \times \varepsilon}\right]\left(\frac{R}{F_i}\right)$$

A_S: The concentration of ^{226}Ra in pCi/L
D_S: Ingrowth factor $(1 - e^{-\lambda t})$, where $\lambda = 0.693/t_{1/2}$
V: Sample volume in L
ε: Counting efficiency for γ-rays under consideration
R: Net counts per s for the gamma-ray under consideration.
F_i: Branching ratio of γ-rays under consideration: 0.46 for 609.1.

$$\sigma = \frac{\sqrt{N}}{t} = \sqrt{\left(\frac{N}{t^2}\right)} = \sqrt{\frac{r}{t}}$$

Diab, H. M.; Abdellah, W. M., "Validation of ^{222}Ra and ^{228}Ra Measurements in Water Sample Using Gamma Spectrometric Analysis." *Journal of Water Resource and Protection*, 2013, 5, 53–57.

Conclusions

- Current methods may be recommended for qualifying of radionuclides in flowback/produce water due to limitations
- Quantifying radionuclides can be done via Gamma Spectroscopy
- The limitations on running via Gamma Spectroscopy are:
  - Elevated lower limits of detection (can be lowered by increasing run times)
  - Natural occurring Uranium can interefer with the Ra-226 line (@ 186 keV)

Conclusions (cont'd)

- (cont'd) Limitations on running via Gamma are:
  - Increased sample turn around time due to prolonged instrument run time & ingrow time (28 day ingrow time for Ra-226)
  - Samples *may need* to be completely homogeneous
    - May require dilution with propylene glycol !
  - Separation may be required/ will separation be needed in order to quantify