

# TestAmerica

THE LEADER IN ENVIRONMENTAL TESTING

## Radiochemical Analytical Challenges with Hydrofrac Fluids

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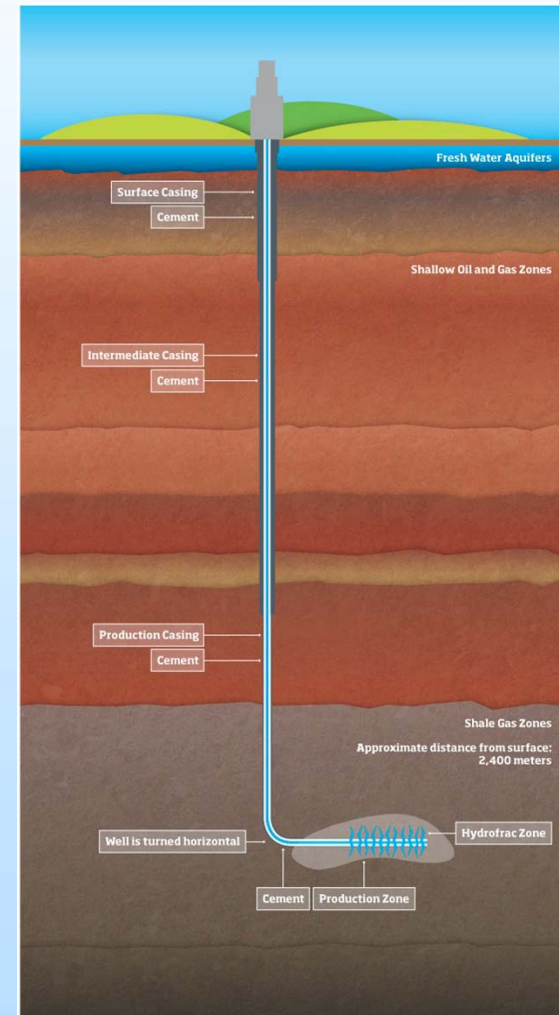
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- **Relatively High TDS**  
(some >250,000 mg/L)
  - ~ Barium (>4,000 mg/L)
  - ~ Calcium (>31,000 mg/L)
  - ~ Strontium (>2,000 mg/L)
  - ~ Iron (>100 mg/L)



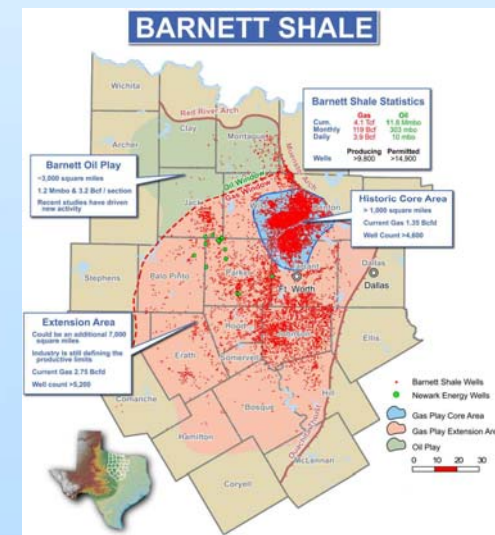
- **Gross Alpha/Beta**  
(EPA 900.0/SW846 9310)
  - ~ “Rough” screening
  - ~ Mass on planchet limited to 100 mg for alpha
  - ~ High solids leads to reduced aliquot and counting efficiency
  - ~ EPA 900.1/SM 7110C can help, but ...





- **Radium Co-precipitation**

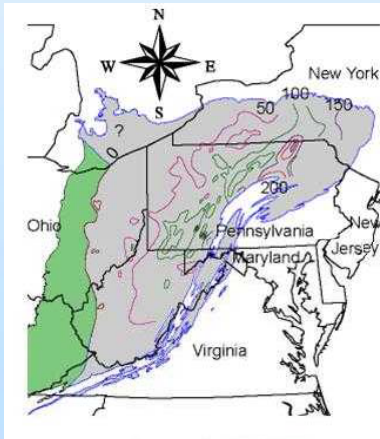
- ~ Most “traditional” precipitation chemistry methods employ sulfate co-precipitation
- ~ Various Pb/Sr/Ba concentrations added
- ~ EDTA cleanup
- ~ Eventually barium sulfate
  - carrier for chemical recovery calculation
  - ~30 mg barium



- **Interferences**

- ~ TDS and Ba/Ca/Sr all cause problems

- General competition in chemistry
- Large qty of barium sulfate precipitate



- Spoils gravimetric chemical recovery
- For GFPC creates flaking issue
- For GFPC increases self-absorption

- **Possible Solutions**
  - ~ Reduce aliquot (increases MDC)
  - ~ Ba-133 as tracer for chemical yield
    - Still have large qty of precipitate
  - ~ Use “non-traditional” method
    - Gamma Spectroscopy (direct count)
    - Gamma Spectroscopy (Ga. Tech method)

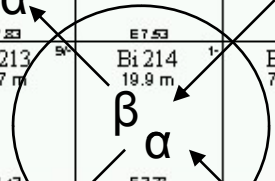
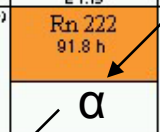
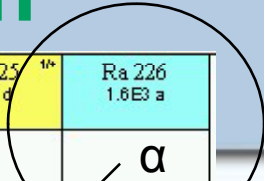
- Ra-226 has one weak gamma emission
  - ~ 3% abundance at 186 keV
- U-235 has several gamma emissions
  - ~ 11% at 144 keV
  - ~ 54% at 186 keV

**U-235 is large interference for Ra-226!!**



# Ra-226 Decay Chain

Ra 215 <sup>(5+)</sup> 1.60 ms	Ra 216 1.8E-7 s	Ra 217 <sup>(5+)</sup> 1.6E-6 s	Ra 218 1.4E-5 s	Ra 219 <sup>(7+)</sup> 10.0 ms	Ra 220 23.0 ms	Ra 221 <sup>5+</sup> 28.0 s	Ra 222 38.0 s	Ra 223 <sup>3+</sup> 11.4 d	Ra 224 87.8 h	Ra 225 <sup>1+</sup> 14.8 d	Ra 226 1.6E3 a
E826	E953	E916	E856	E813	E780	E629	E668	E556	E579	E367	E427
<sup>(2-)</sup> Fr 214 <sup>(1-)</sup> 3.40 ms   5.00 ms	Fr 215 <sup>5+</sup> 9.0E-8 s	Fr 216 <sup>(1-)</sup> 7.0E-7 s	Fr 217 <sup>5+</sup> 2.2E-6 s	Fr 218 <sup>(1-)</sup> 7.0E-4 s	Fr 219 <sup>5+</sup> 20.0 ms	Fr 220 <sup>1+</sup> 27.5 s	Fr 221 <sup>5+</sup> 4.80 m	Fr 222 <sup>2-</sup> 14.8 m	Fr 223 <sup>(3-)</sup> 21.8 m	Fr 224 <sup>(1-)</sup> 160 s	Fr 225 <sup>(3-)</sup> 3.00 m
E859	E954	E918	E847	E801	E745	E620	E646	E203	E115	E282	E187
Rn 213 <sup>(5+)</sup> 25.0 ms	Rn 214 2.7E-7 s	Rn 215 <sup>5+</sup> 2.3E-6 s	Rn 216 45.0 s	Rn 217 <sup>5+</sup> 5.4E-4 s	Rn 218 35.0 ms	Rn 219 <sup>5+</sup> 3.96 s	Rn 220 55.6 s	Rn 221 <sup>(7+)</sup> 25.0 m	Rn 222 91.8 h	Rn 223 <sup>(7-)</sup> 43.0 m	Rn 224 107 m
E824	E921	E884	E820	E789	E726	E696	E641	E122	E599		
<sup>(2-)</sup> At 212 <sup>(1-)</sup> 122 ms   315 ms	At 213 <sup>5+</sup> 1.1E-7 s	At 214 <sup>1-</sup> 2.0E-6 s	At 215 <sup>5+</sup> 1.0E-4 s	At 216 <sup>(1-)</sup> 3.0E-4 s	At 217 <sup>5+</sup> 32.0 ms	At 218 <sup>(2-)</sup> 2.00 s	At 219 54.0 s				
E783	E926	E859	E818	E796	E720	E627	E639				
<sup>(25+)</sup> Po 211 <sup>5+</sup> 25.5 s   520 ms	<sup>(18+)</sup> Po 212 45.0 s   3.0E-7 s	Po 213 <sup>5+</sup> 4.2E-6 s	Po 214 1.0E-4 s	Po 215 <sup>5+</sup> 2.00 ms	Po 216 150 ms	Po 217 10.0 s	Po 218 183 s				
E780	E856	E854	E783	E753	E691	E696	E612				
<sup>5-</sup> Bi 210 <sup>1-</sup> 3.5E5 a   5.01 d	Bi 211 <sup>5+</sup> 130 s	Bi 212 <sup>(1-)</sup> 60.6 m	Bi 213 <sup>5+</sup> 45.7 m	Bi 214 <sup>(1-)</sup> 19.9 m	Bi 215 7.40 m						
E116	E675	E226	E143	E327	E226						
Pb 209 <sup>5+</sup> 3.25 h	Pb 210 20.4 a	Pb 211 <sup>5+</sup> 36.1 m	Pb 212 10.6 h	Pb 213 <sup>(5+)</sup> 10.2 m	Pb 214 26.8 m						
E644	E064	E137	E574	E207	E107						
Tl 208 <sup>5+</sup> 186 s	Tl 209 <sup>(1+)</sup> 132 s	Tl 210 <sup>(5+)</sup> 79.2 s									
E500	E396	E548									



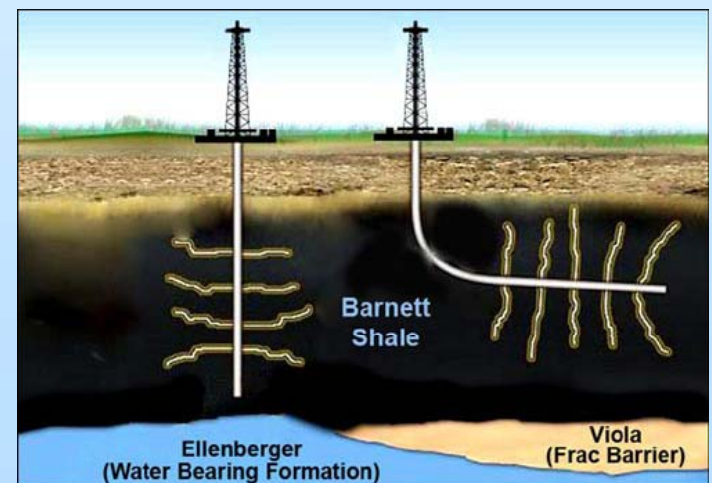
- First progeny of Ra-226, Rn-222 (gas), can escape matrix.
- Seal in a geometry, then allow for decay chain to ingrow
- Measure Bi-214 (46% gamma at 609 keV)



## Secular equilibrium

- ~ Half-life of Ra-226 (1600 years) is much greater than of Rn-222 (91.8 hrs)
- ~ Rest of decay chain down to Pb-210 has short half-life (<30 min.)
  - o 7 days = 72% ingrowth
  - o 14 days = 92% ingrowth
  - o 21 days = 98% ingrowth

- **Direct Count (No Preparation)**
  - ~ Place sample (e.g. 1L) in geometry
  - ~ Count after ingrowth
  - ~ MDC of 30-50 pCi/L
  - ~ Ra-226/228 concentration:
    - Flowback duration
    - Ba content



- Georgia Tech Research Institute (Bernd Kahn, Robert Rosson)
  - ~ Coprecipitate Radium with barium sulfate
  - ~ Modify by adding Ba-133 as tracer
  - ~ Allow ingrowth (can use any time)
  - ~ Ra-226, Ra-228, and Ba-133 recovery from single analysis
  - ~ Should allow for lower MDC (<5 pCi)

## Other Considerations

- **What is actual sample matrix?**
- **What is ultimate goal of analysis?**
- **What are regulatory requirements?**
- **??????**



# Questions?

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