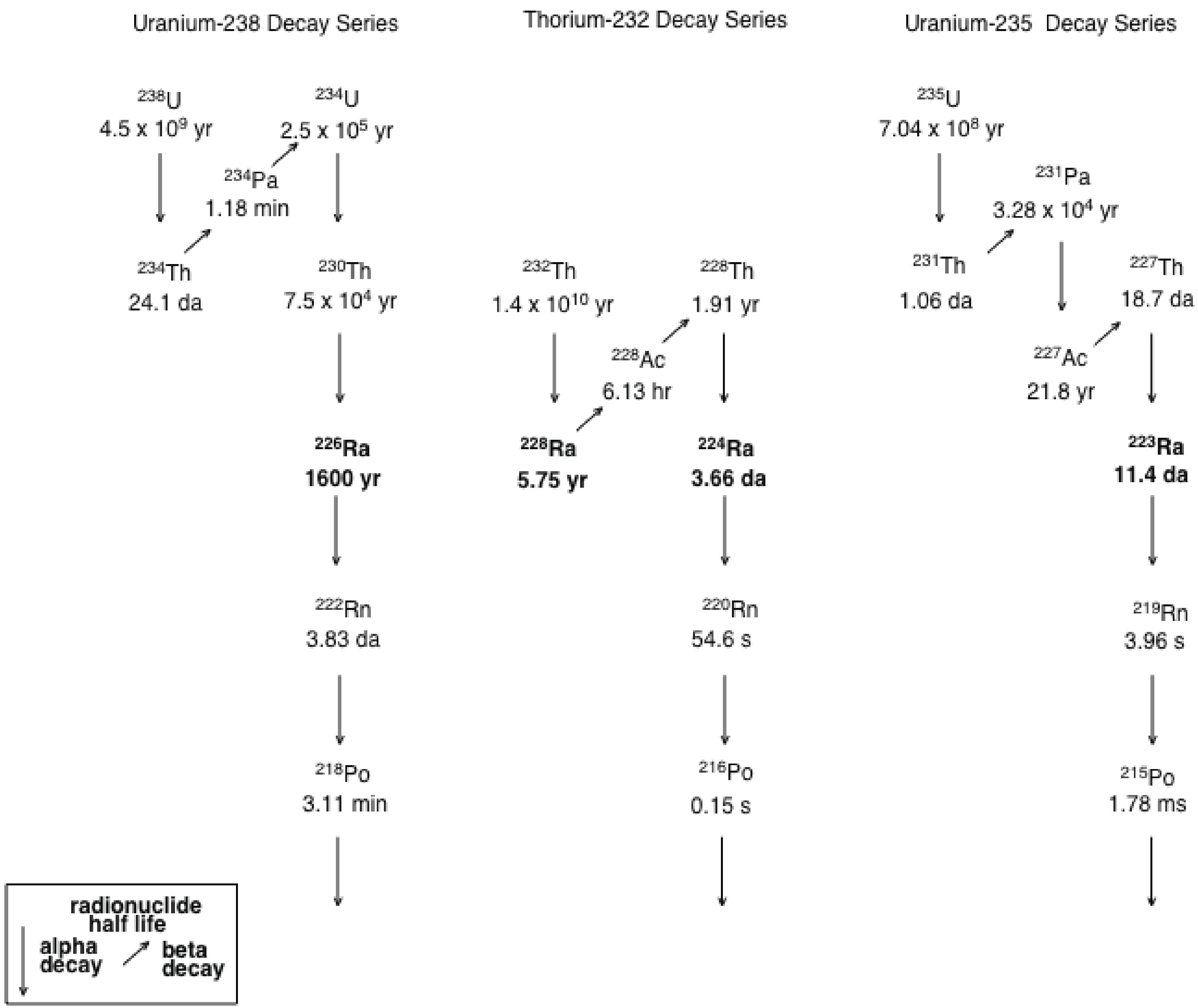
Measurements Using RaDeCC (Radium Delayed Coincidence Counter)

Willard S. Moore
Department of Earth & Ocean Sciences
University of South Carolina
Columbia, SC, USA
moore@geol.sc.edu



Uranium-238 Decay Series
Thorium-232 Decay Series
Uranium-235 Decay Series
238U 4.5 x 10^9 yr
234U 2.5 x 10^5 yr
234Pa 1.18 min
234Th 24.1 da
230Th 7.5 x 10^4 yr
226Ra 1600 yr
222Rn 3.83 da
218Po 3.11 min
232Th 1.4 x 10^10 yr
228Th 1.91 yr
228Ac 6.13 hr
228Ra 5.75 yr
224Ra 3.66 da
220Rn 54.6 s
216Po 0.15 s
235U 7.04 x 10^8 yr
231Pa 3.28 x 10^4 yr
231Th 1.06 da
227Th 18.7 da
227Ac 21.8 yr
223Ra 11.4 da
219Rn 3.96 s
215Po 1.78 ms
radionuclide
half life
alpha decay
beta decay

Sample Collection and Processing

Procedure for water samples

Pump a sample into a container.

Measure salinity; collect subsamples (Ba, nutrients, alkalinity, etc.).

Concentrate radium isotopes on a column of MnO_2-coated fiber.

Wash and partially dry the Mn-fiber.


Waters with higher radium activity
26 L
AQUA-TAINER
AQUA-TAINER

Measuring ^{223}Ra and ^{224}Ra

Giffin, C., Kaufman, A., Broecker, W.S., 1963. Delayed coincidence counter for the assay of actinon and thoron. J. Geophys. Res. 68, 1749–1757.

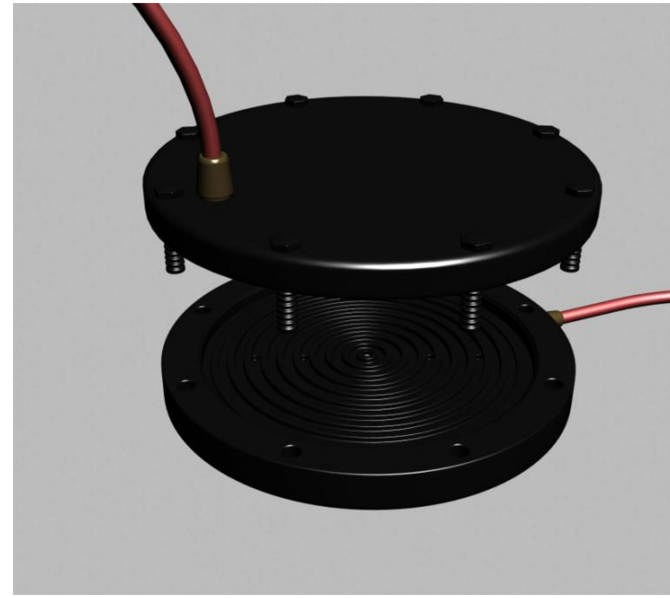
Moore, W.S., Arnold, R., 1996. Measurement of ^{223}Ra and ^{224}Ra in coastal waters using a delayed coincidence counter. J. Geophys. Res. 101, 1321–1329.

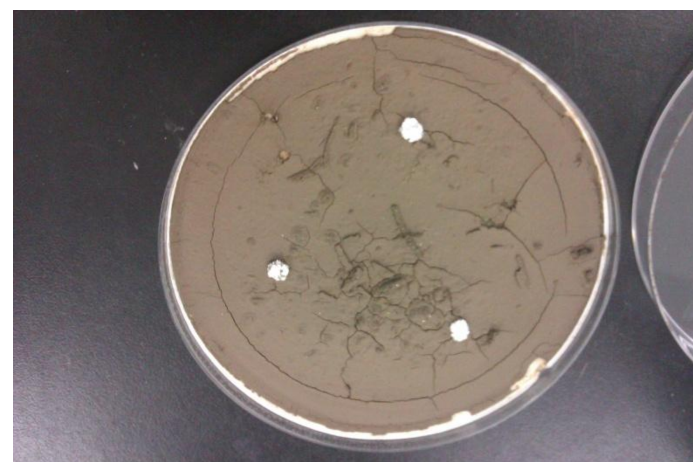
Can also measure ^{224}Ra in sediment samples

RaDeCC system (with an array of 6 counters)

Cai, Pinghe, Xiangming Shi, W. S. Moore, Minhan Dai, Measurement of ^{224}Ra:^{228}Th disequilibrium in coastal sediments using a delayed coincidence counter. Marine Chemistry, 2012.

Sample Chamber (vol = 50 ml)





Sediment sample

The technique had its beginnings in Ernest Rutherford's lab 100 years a

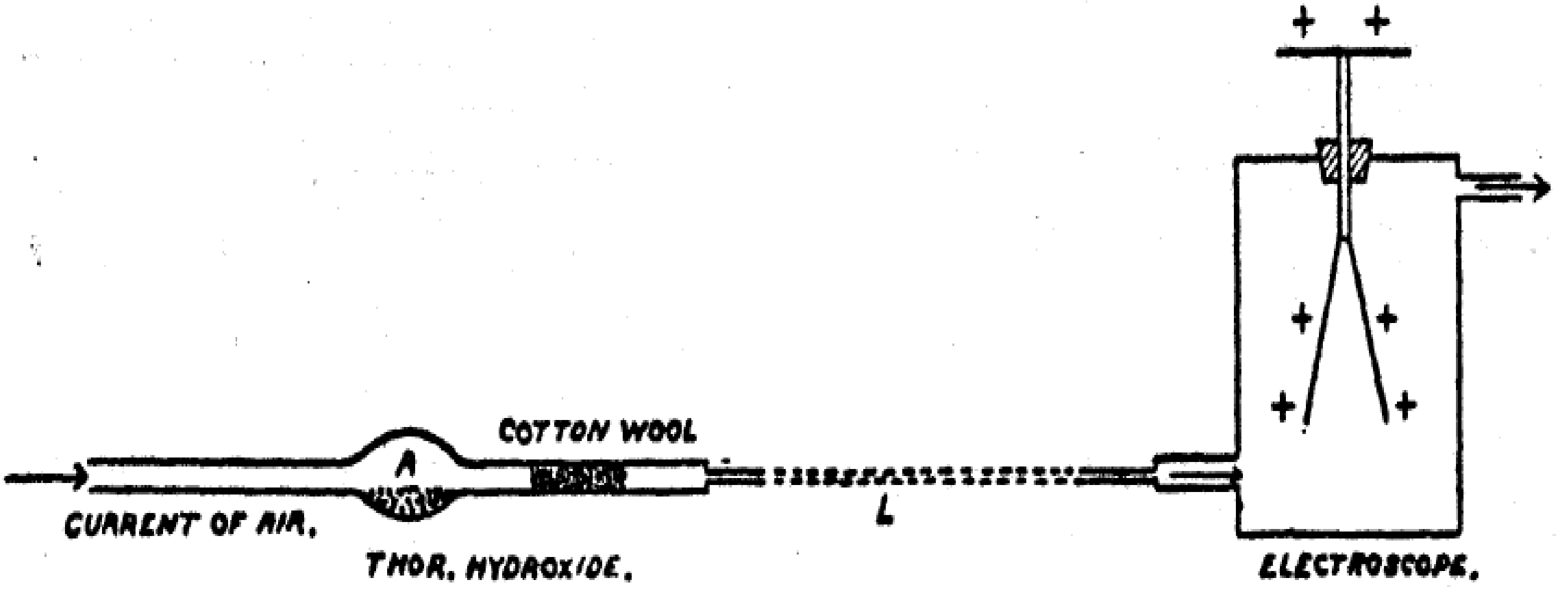
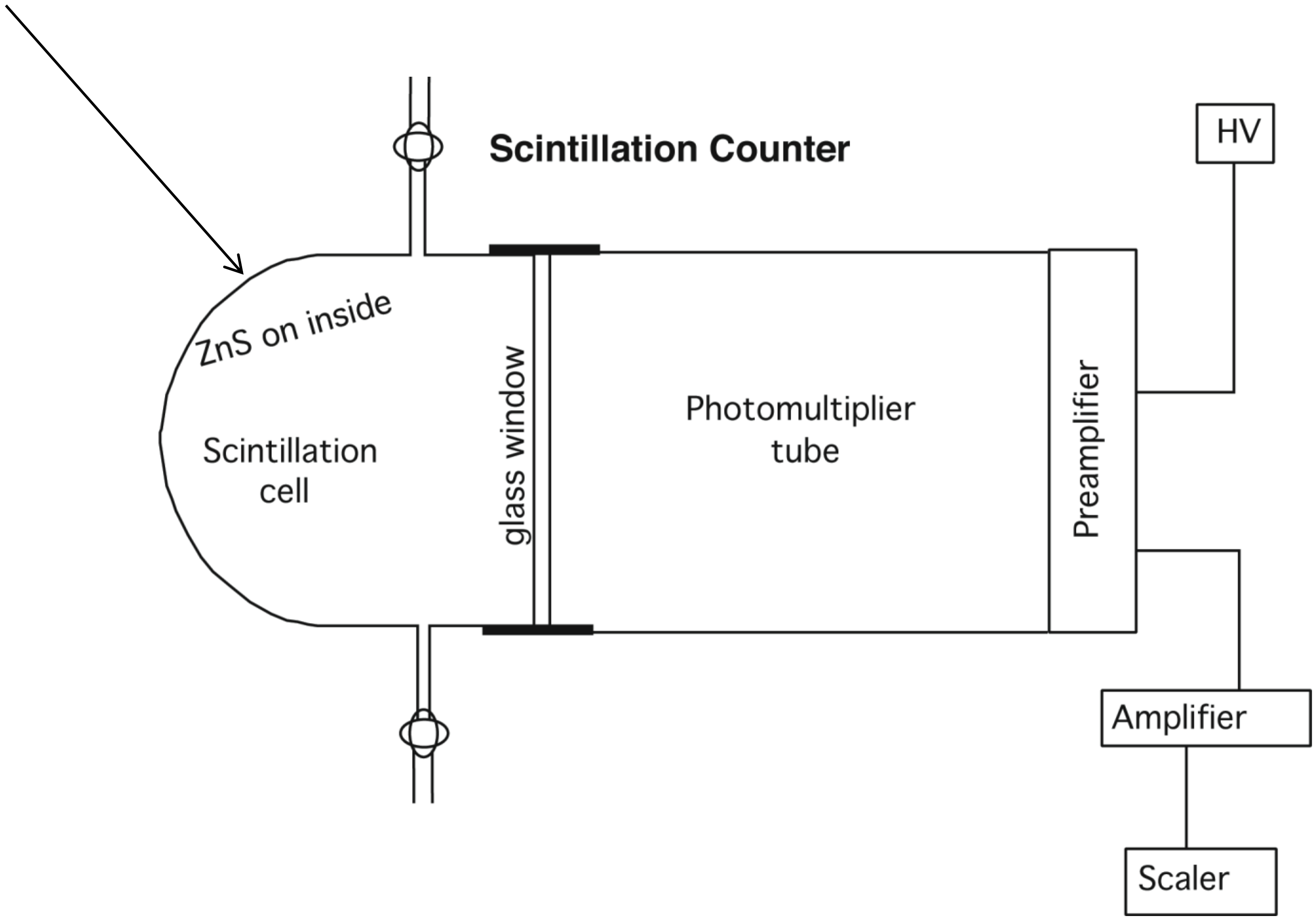


FIG. 11.
Discharging power of the thorium emanation.

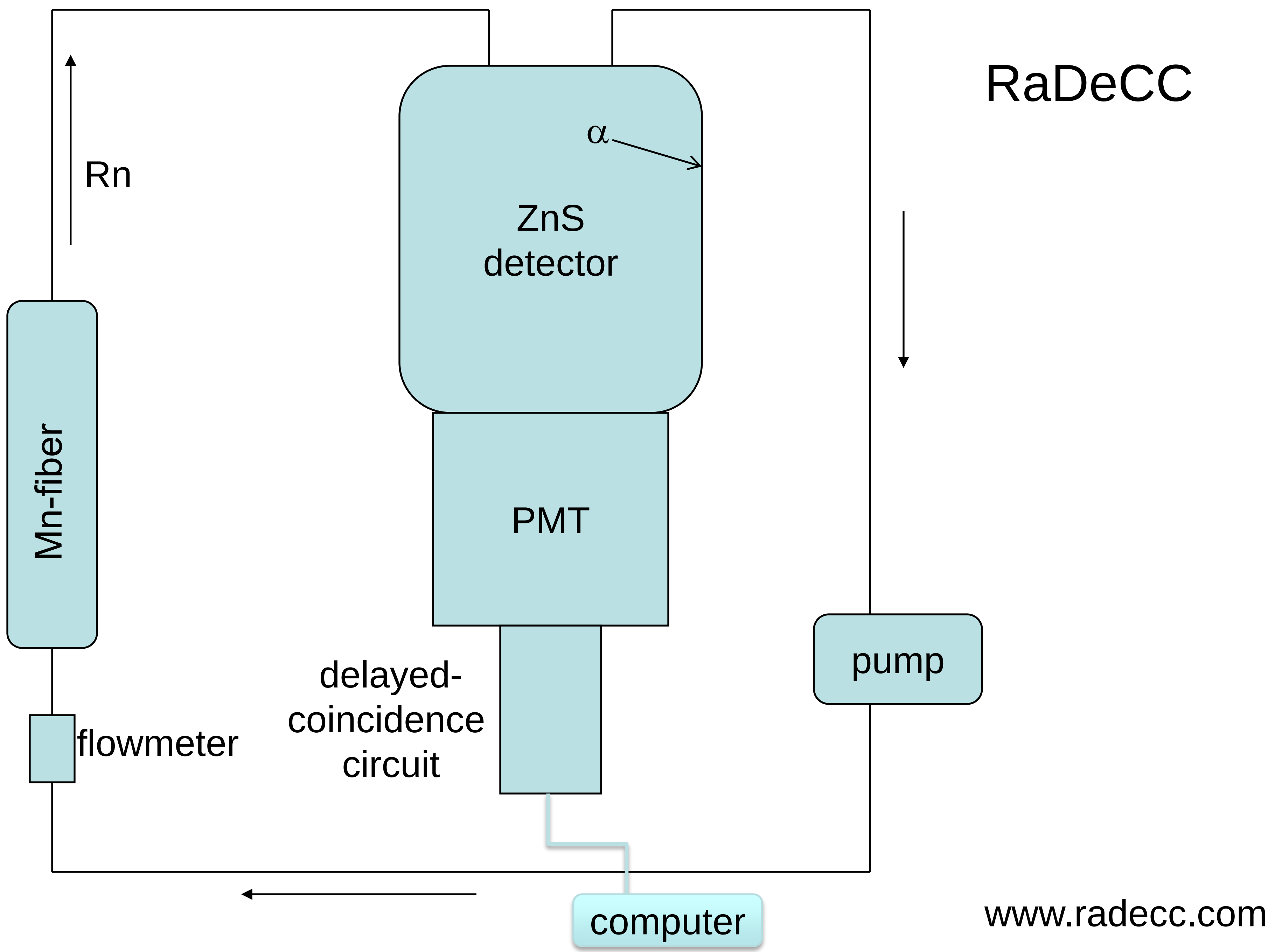
(^{220}Rn, half life = 54 sec)

From Ernest Rutherford: <u>Radioactive Transformations</u> (1908)

The Lucas cell



Henry Lucus, 1957

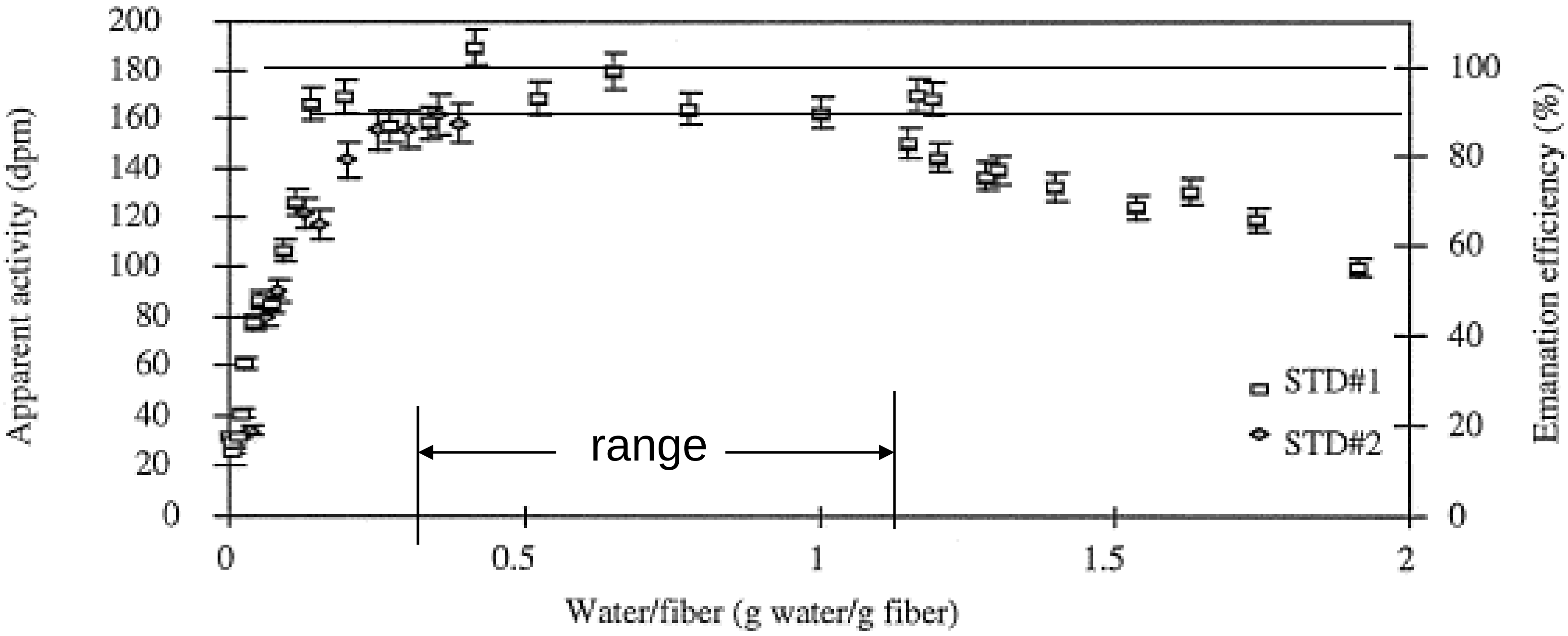

RaDeCC
α
Rn
ZnS
detector
Mn-fiber
PMT
pump
delayed-
coincidence
circuit
flowmeter
computer
www.radecc.com

Does all of the Rn escape from the fiber?

In a strict sense all of the Rn does not have to escape to make the technique reliable. Instead the same fraction must escape from the sample as escapes from the standard. The fraction that escapes must not change with time and must not vary sample-to-sample.

We know that some moisture on the fiber surface is required to prevent the recoiled Rn from embedding in adjacent particles of MnO_2. Too much water reduces the emanation and may reduce the cell efficiency.

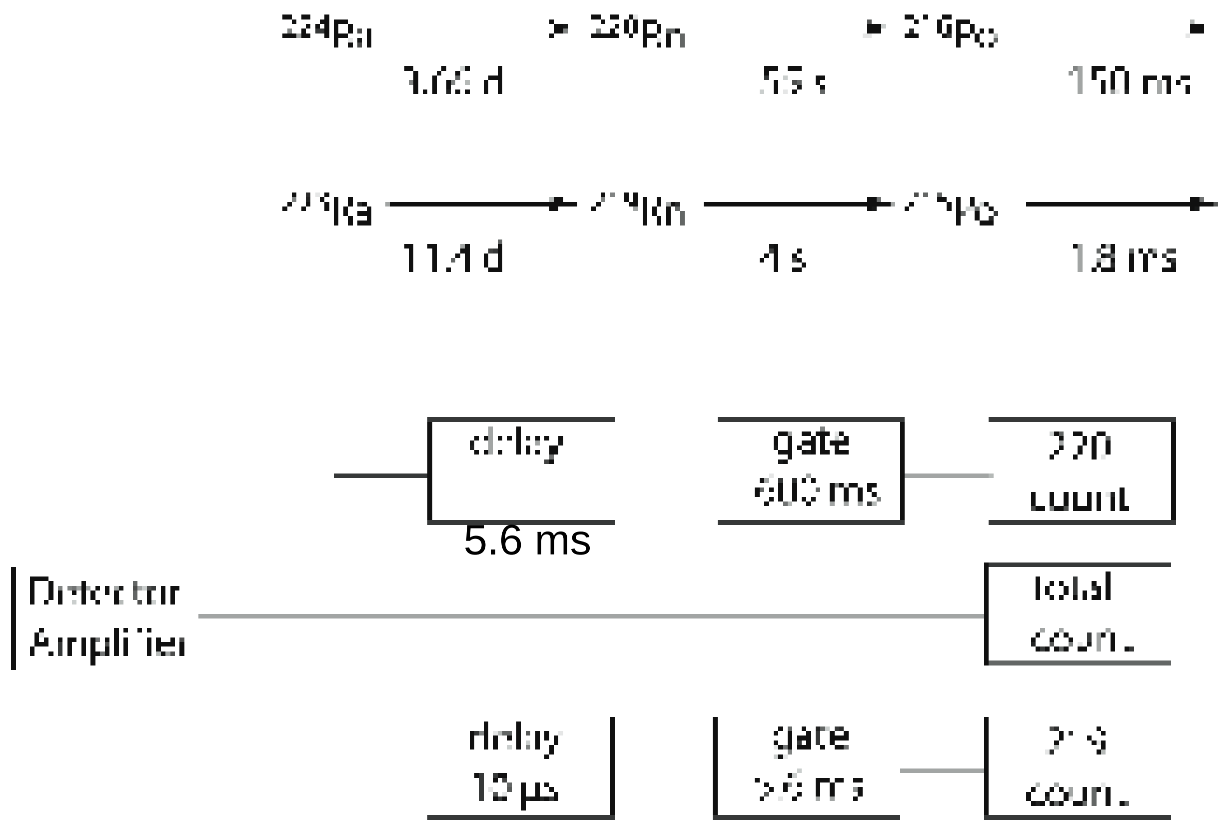
Effect of water content on the emanation of ^{220}Rn from Mn-fiber



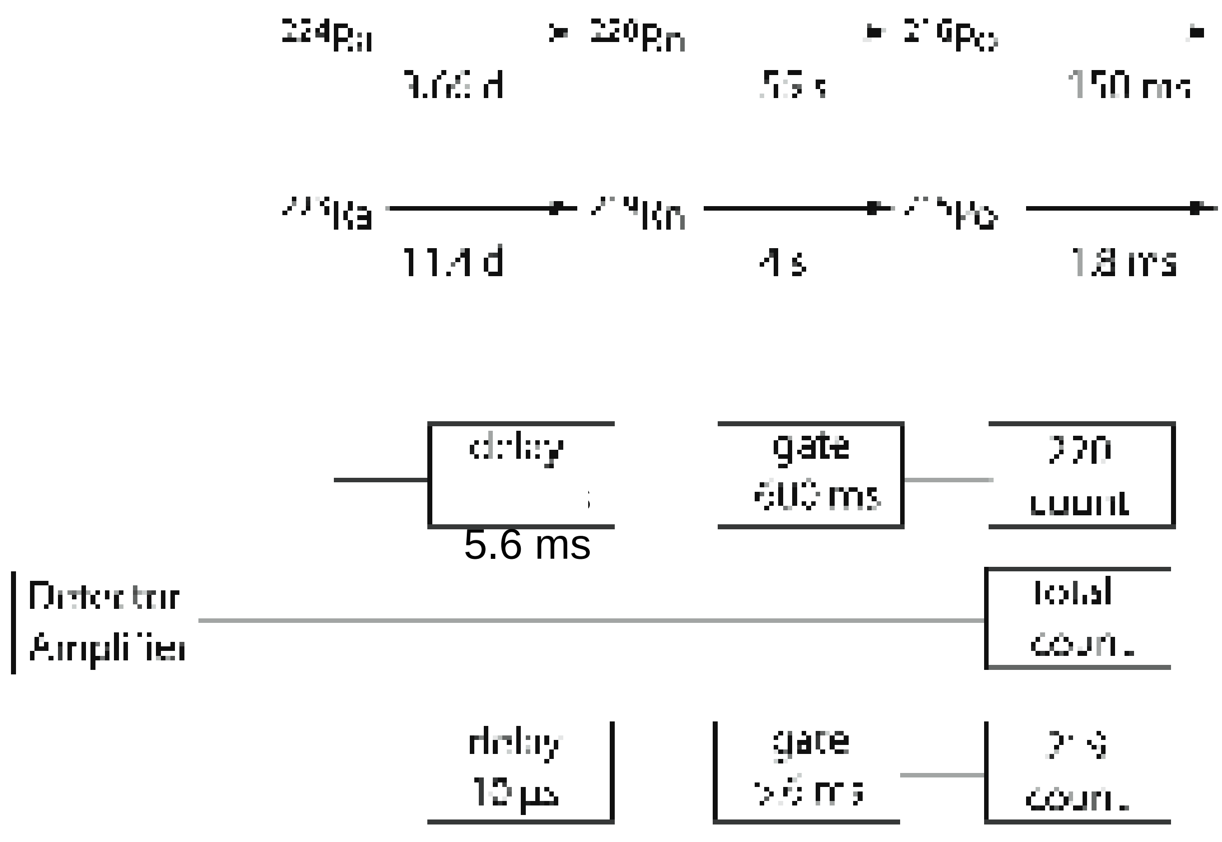
This implies that 15 gms of dry fiber should contain 7-17 gmswater.

Sun and Torgersen (1998) Marine Chem. 62, 299-306

Delayed Coincidence Counter



Delayed Coincidence Counter



During the 5.6 ms the 219 gate is open, about 2.5% of the ^{220}Rn decays are expected to occur. The 219 corrections take this into account.

If an atom of radon decays in the counting cell and the alpha particle strikes the wall, it will produce a flash of light. This light is picked up by the photomultiplier tube, converted to an electrical signal, and passed to the chance coincidence circuit. This signal is recorded in the total counts window (Total). After this signal is delayed for 10 ms in the 220 circuit or 5.6 µs in the 219 circuit, it opens a gate in each circuit, then the signal dies.

If a second signal occurs it will also be delayed and then be passed to the window. If the second signal after delay occurs within the time constant of each window (600 ms for 220 and 5.6 ms for 219), it will register as a count in the appropriate window. However, because all signals passed to the 220 circuit are delayed for 10 ms, any signal due to ^{215}Po will die before it can pass through the 220 window.

Likewise, very few signals (2.5%) from ^{216}Po decay will occur within the time constant of the 219 window.

There is always the possibility that 2 Rn atoms will decay while the windows are open. These are called chance coincidence counts and are estimated and eliminated based on statistics.

Measuring ^{223}Ra and ^{224}Ra via delayed coincidence counting

a. Flushing with helium-Why He?
b. Flow rate of helium
c. Checking for leaks
d. Chance coincidence events
e. Standards
f. Buildup of ^{222}Rn
g. Strategy for high activity samples
h. Second and third runs
i. Corrections for ^{228}Th and ^{227}Ac

Chance coincidence events

The 220 window is open for 600 ms. If a second decay occurs during this period it will register in the 220 window. This is called a chance coincidence count. The effect is much less for 219 because this window is only open for 5.6 ms

Total cpm	220 cc cpm 600 msec	219 cc cpm 5.6 msec
1	0.01	0.0001
4	0.15	0.001
10	0.91	0.009
20	3.33	0.037
50	16.7	0.232

Chance correction equations for ^{224}Ra and ^{223}Ra

From Moore and Arnold 1964

$$\text{220 chance coinc. (cpm)} = \frac{(\text{total cpm - 220 cpm - 219 cpm})^2 \times 0.01\ \text{min}}{1 - (\text{total cpm - 220 cpm - 219 cpm}) \times 0.01\ \text{min}} \quad (4)$$

$$\text{219 chance coinc. (cpm)} = \frac{(\text{total cpm - 220 cpm - 219 cpm})^2 \times 9.5 \times 10^{-5}\ \text{min}}{1 - (\text{total cpm - 220 cpm - 219 cpm}) \times 9.5 \times 10^{-5}\ \text{min}} \quad (5)$$

Giffin, C., Kaufman, A., Broecker, W.S., 1963. Delayed coincidence counter for the assay of actinon and thoron. J. Geophys. Res. 68, 1749–1757.

Moore, W.S., Arnold, R., 1996. Measurement of ^{223}Ra and ^{224}Ra in coastal waters using a delayed coincidence counter. J. Geophys. Res. 101, 1321–1329.

Calibration (i.e. Efficiency Determination)

Radionuclide measurements are almost always made in conjunction with the measurement of a standard supplied by a national lab (NIST or EPA). The standard is used to calibrate the efficiency of the instrument and thus translate cpmto dpm.

For example if a standard with a known activity of 2396 dpm yielded 796.0 cpm in the counter being calibrated, the efficiency of the counter would be 33.20%. A sample that counted 123.0 cpmin this counter would have an activity of 370.2 dpm. Of course we must also propagate the uncertainty of the standard itself and the statistical error associated with the measurement of the standard in the counter. These errors in calibration usually add another 2-3% error to the statistical uncertainty.

Calibration (i.e. Efficiency Determination)

It is impractical to obtain a true standard for a short-lived isotope. To calibrate a system to measure short-lived isotopes, we must use standards containing long-lived parents. For ^{224}Ra, we use ^{232}Th with daughters in equilibrium; for ^{223}Ra we use ^{227}Ac with daughters in equilibrium. However there is no source of calibrated ^{227}Ac.

Standards

$^{232}Th \rightarrow {}^{228}Ra \rightarrow {}^{228}Th \rightarrow {}^{224}Ra$

$^{227}Ac \rightarrow {}^{278}Th \rightarrow {}^{223}Ra$

Each standard solution is added to sea water adjusted to pH = 6 with NH_4OH and passed through a Mn-fiber column that has been washed well and pretreated with pH = 6 sea water. The effluent is collected and recirculated through the column several times. The column is washed with DI water, partially dried, and immediately measured. If there was incomplete uptake of Th or Ac on the Mn-fiber, the count rate will decrease over the next several days. The standards are remeasured at least 5 times during the first 2 months. Any that are not stable are rejected.

Problems in calibrating RaDeCC systems for ^{223}Ra-^{227}

1. The apparent activity of ^{223}Ra in standards prepared from ^{227}Ac decreases with time (Scholten et al., 2010).

2. Well-calibrated ^{227}Ac solutions are difficult to obtain.

Therefore we utilize the calibration of the 220 channel to calibrate the 219 channel.

Moore, W.S., Fifteen years experience in measuring ^{224}Ra and ^{223}Ra by delayed-coincidence counting. Marine Chemistry, 109, 188-197, 2008.

Willard S. Moore and Pinghe Cai, Calibration of RaDeCC Systems for ^{223}Ra Measurements. Marine Chemistry, 156, 130-137, 2013.

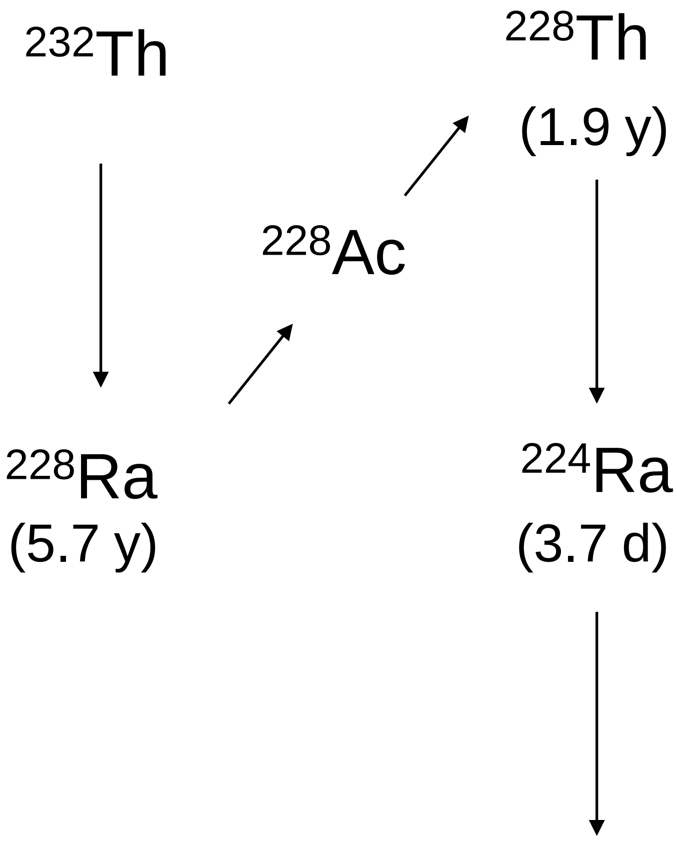
Second, Third and Fourth Runs

After a week the ^{224}Ra activity has decreased by ~75%, but the ^{223}Ra has decreased by only 35%. I usually recount the samples after 7-10 days for a better ^{223}Ra number. The lower ^{224}Ra activity means the 2.5% correction will be reduced considerably.

After 25 days the ^{224}Ra activity will be <1% of the initial activity and ^{224}Ra is essentially supported by ^{228}Th in the sample. Thus, another count at this time will measure ^{228}Th.

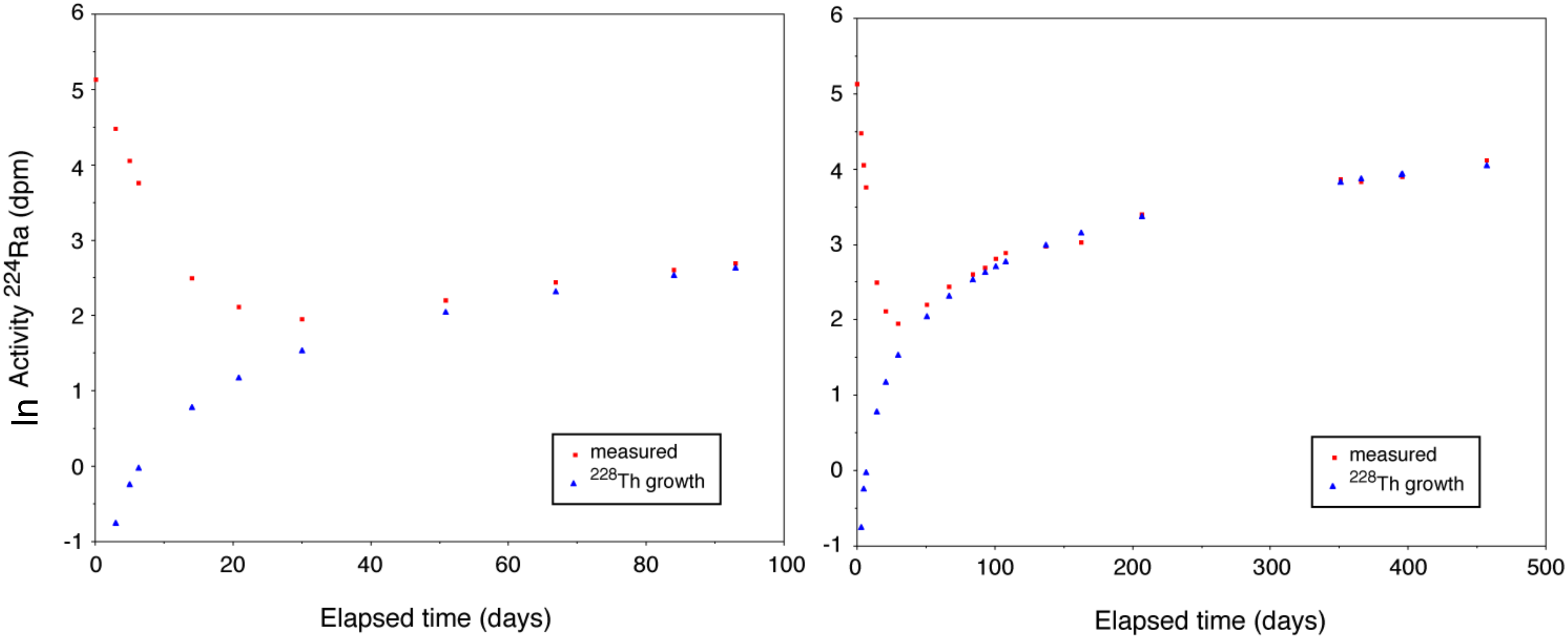
After 80 days the ^{223}Ra activity will be <1% of the initial activity and ^{223}Ra is essentially supported by ^{227}Ac in the sample. Thus, another count at this time will measure ^{227}Ac. Because ^{227}Ac is extremely low in surface water, this 4th count is rarely required.

Measuring ^{228}Ra via ^{228}Th ingrowth on fiber



Time (days)	$^{228}Th/^{228}Ra$ Fraction equilibrium
30	0.03
90	0.09
150	0.14
365	0.30

Results of repeatedly counting a sample from Port Royal Sound



$^{228}Ra \rightarrow ^{228}Th \rightarrow ^{224}Ra$

Conclusions

1. The RaDeCC system provides a effective way to measure ^{223}Ra and ^{224}Ra in water samples.

2. It is also possible to measure ^{224}Ra and ^{228}Th in sediments.

3. Other radionuclides that can be measured include ^{228}Ra, ^{226}Ra, ^{227}Ac.

Additional Materials for Practicals

Calculations

Sample file	Location	coll. date	coll. time	Vol. L	Sal. ppt
TT1-2.5		30-Mar-10	13:28	4	34
TT1-2.5		30-Mar-10	13:28	4	34
TT1-2.5		30-Mar-10	13:28	4	34
TT1-5		30-Mar-10	13:42	4	37.9
TT1-5		30-Mar-10	13:42	4	37.9
TT1-5		30-Mar-10	13:42	4	37.9
TT2-2.5		30-Mar-10	14:28	4	40.6
TT2-2.5		30-Mar-10	14:28	4	40.6
TT2-2.5		30-Mar-10	14:28	4	40.6

info you provide

count file	sys	E 219 coinc	E 220 coinc	E total	count date	count time	count min	cpm 219	cts 219	cpm 220	cts 220	cpm total	cts total	C
"C:\RaDeCC\Data\MR10TT125M	4	0.49	0.54	1.3	31-Mar-10	14:12:03	85.07	0.47	40	6.607	562	15.165	1290	0"
"C:\RaDeCC\Data\MR10TT125M.2	4	0.49	0.54	1.3	7-Apr-10	9:05:47	306.02	0.199	61	1.307	400	4.104	1256	0"
"C:\RaDeCC\Data\MR10TT125M.3	4	0.49	0.54	1.3	26-Apr-10	9:40:56	362.33	0.05	18	0.188	68	1.206	437	0"
"C:\RaDeCC\Data\MR10TT15M	2	0.4	0.46	1.19	31-Mar-10	14:11:57	84.83	0.695	59	9.301	789	22.255	1888	0"
"C:\RaDeCC\Data\MR10TT15M.2	2	0.4	0.46	1.19	7-Apr-10	9:05:42	306.03	0.314	96	2.052	628	6.689	2047	0"
"C:\RaDeCC\Data\MR10TT15M.3	2	0.4	0.46	1.19	26-Apr-10	9:40:48	362.37	0.052	19	0.149	54	1.416	513	0"
"C:\RaDeCC\Data\MR10TT225M	1	0.42	0.48	1.25	31-Mar-10	14:11:55	84.63	1.607	136	20.559	1740	42.938	3634	0"
"C:\RaDeCC\Data\MR10TT225M.2	1	0.42	0.48	1.25	7-Apr-10	9:05:39	306.03	0.343	105	3.509	1074	9.339	2858	0"
"C:\RaDeCC\Data\MR10TT225M.3	1	0.42	0.48	1.25	26-Apr-10	9:40:44	362.4	0.03	11	0.116	42	1.785	647	0"

information from summary file

Tot cpm bkgd	decay hours	decay 224	decay 223	y 220 c. c.	corr 220	y 219 cc	corr 219	final 220	decay corr dpm 219	decay corr dpm 220	decay corr dpm 220 Tot	220/cc	tot/bkgd
0.84	25	0.818	0.938	0.7	5.850	0.007	0.312	5.848	0.678	13.2	12.7	9.3	18.1
1.147	190	0.223	0.618	0.1	1.193	0.001	0.166	1.192	0.548	9.0	8.8	18.9	3.6
0.912	647	0.006	0.194	0.0	0.134	0.000	0.044	0.133	0.467				
0.84	25	0.820	0.938	1.7	7.543	0.018	0.482	7.537	1.285	19.9	20.6	5.4	26.5
0.679	190	0.223	0.618	0.2	1.812	0.002	0.264	1.810	1.067	16.9	20.9	10.5	9.9
0.902	647	0.006	0.195	0.0	0.089	0.000	0.048	0.089	0.611				
1.188	24	0.825	0.940	5.4	15.068	0.064	1.156	15.030	2.929	38.0	37.6	3.8	36.1
0.778	189	0.225	0.620	0.3	3.145	0.003	0.258	3.144	0.990	28.8	29.2	11.0	12.0
0.997	646	0.006	0.195	0.0	0.044	0.000	0.027	0.044	0.325				

info you provide

calculated by spreadsheet

Ra223 dpm/L	Ra223 counts	exRa224 dpm/L	final Ra223 dpm/L	Th228 dpm/L
0.170	40	3.13	0.137	0.06
0.137	61			
				0.06
0.321	59	5.11	0.267	0.04
0.267	96			
				0.04
0.732	136	9.38	0.247	0.01
0.247	105			
				0.01

Excel Worksheet for Standard Runs

H-7 = 22.63 dpm ^{232}Th;   A-8 = 22.59 dpm ^{227}Ac

Sample file	sys	E 219	E 220	E total	count date	count time	count min	cpm 219	cts 219	cpm 220	cts 220	cpm total	cts total	com
H-7STD1.M1	1	0.45	0.5	1.29	29-Mar-06	10:13	74.9	0.64	48	13.64	1021	28.74	2152	0"
H-7STD1.M2	1	0.45	0.5	1.29	29-Mar-06	11:34	87.9	0.41	36	13.28	1167	28.57	2510	0"
H-7STD1.M3	1	0.45	0.5	1.29	30-Mar-06	12:14	101.3	0.47	48	13.50	1367	28.69	2905	0"
A-8.STD4.A4	4	0.49	0.54	1.25	14-Apr-06	10:09	76.4	11.05	844	4.54	347	30.84	2356	0"
A-8.STD4.M1	4	0.49	0.54	1.25	4-May-06	9:52	83.4	10.76	897	5.18	432	30.28	2524	0"

Tot cpm bkgd	y 220 cc	corr 220	y 219 cc	corr 219	final 220	Eff. 220	Eff. 219	Eff. total
1.19	2.45	11.19	0.02	0.33	11.19	0.49		1.22
1.19	2.60	10.68	0.02	0.12	10.68	0.47		1.21
1.78	2.54	10.96	0.02	0.17	10.96	0.48		1.19
1.17	2.74	1.80	0.02	10.98	-2.66		0.49	1.31
1.17	2.40	2.78	0.02	10.67	-1.40		0.47	1.29

Apparent system efficiency

Efficiency = corrected cpm/dpm

Second, Third and Fourth Runs

After a week the ^{224}Ra activity has decreased by ~75%, but the ^{223}Ra has decreased by only 35%. I usually recount the samples after 7-10 days for a better ^{223}Ra number. The lower ^{224}Ra activity means the 2.5% correction will be reduced considerably.

After 25 days the ^{224}Ra activity will be <1% of the initial activity and ^{224}Ra is essentially supported by ^{228}Th in the sample. Thus, another count at this time will measure ^{228}Th.

After 80 days the ^{223}Ra activity will be <1% of the initial activity and ^{223}Ra is essentially supported by ^{227}Ac in the sample. Thus, another count at this time will measure ^{227}Ac. Because ^{227}Ac is extremely low in surface water, this 4th count is rarely required.

Why do we need to know ^{228}Th?

Assume our sample contains 9 dpm total ^{224}Ra and 1 dpm^{228}Th, or 8 dpm excess ^{224}Ra.

If the sample is run 3.7 days after collection the initial ^{224}Ra will decrease to 4.5 dpm and 0.5 dpm^{224}Ra will be generated by ^{228}Th decay, so total ^{224}Ra will now be 5 dpm.

The calculations in column AF or AG will correct final ^{224}Ra back to 9 dpm.

AF: [final 220 1st count/eff – (final 220 3rd count/eff)*(1-224decay 1st count)]/224 decay 1st ct

= [5 – (1 - 0.5)] /0.5 = 9

Finally we must correct the total ^{224}Ra for the ^{228}Th supported amount to yield 8 dpm excess ^{224}Ra.

decay hours	decay 224	decay 223	y 220 c. c.	corr 220	y 219 cc	corr 219	final 220	decay corr dpm 219
71	0.572	0.836	3.196	11.800	0.036	0.942	11.77	2.30
359	0.059	0.403	0.198	1.597	0.002	0.343	1.59	1.89
741	0.003	0.153	0.034	0.544	0.000	0.088	0.54	1.17

AF	AG							
decay corr dpm 220	decay corr dpm 220 Tot	220/cc	tot/bkgd	Ra223 dpm/L	Ra223 counts	exRa224 dpm/L	final Ra223 dpm/L	Th228 dpm/L
37.40	39.42	4.71	29.43	0.58	93	9.61	0.47	0.25
35.98	55.16	9.30	4.39	0.47	99			
								0.25

Must correct for ^{224}Ra that has been produced by ^{228}Th decay on the fiber
after sample collection. Assume that the uptake efficiency of Ra and Th are the same.

[final 220 1st count/eff - (final 220 3rd count/eff)*(1-224decay 1st count)]/224decay 1st ct

Finally must correct for the amount of ^{224}Ra in the water column that is

Corrections for Chance Coincidence Events

from Giffin et al., 1963

x = count rate of random single pulses recorded in the "before-coincidence" (bc or Total) register (events/sec)

t_g = time constant, the length of time the window is open per event (sec/event), set by user

y = count rate of chance coincidence events, i.e. events that occur within the time constant of the circuit and record in the "after-coincidence" (ac) register (events/sec)

x-y = rate at which the window opens (ac events do not open the window) (events/sec)

$(x-y)t_g$ = fraction of "on" time. This is equal to the fraction of window openings that result in a pulse recording in the ac register. Note the units cancel.

y/x = fraction of random single pulses that record in the ac register. **This must equal the fraction of "on" time.**

$(x-y)t_g = y/x$ (1)

Solve for y:

$$y = \frac{x^2 t_g}{1 + x t_g} \qquad (2)$$

$x = (bc) - [(ac) - y] = bc-ac + y$

$x - y = bc - ac$

From (1):

$y/x = (bc-ac)t_g$

$y = (bc-ac)t_g x = (bc-ac)[(bc-ac) + y]t_g = (bc-ac)^2 t_g + (bc-ac)y t_g$

$$y = \frac{(bc-ac)^2 t_g}{1 - [(bc-ac)t_g]} \qquad (3)$$

Correction for 220 events in the 219 Channel

A 220 event will open the 220 and 219 windows. The 219 window opens for 5.6 msec. During this interval there is a chance the coincident 220 event (^{216}Po decay) will occur. This chance is equal to:

cpm 220 (1 - exp $-\lambda_{216}$t) where λ_{216} is 0.0046 msec^{-1} and t is 5.6 msec.

$$(1 - \exp -\lambda_{216}t) = 0.0255 \qquad (6)$$

For example if the true 220 count rate is 20 cpm, the correction is 0.51 cpm

Corrections for Coincidence 219 Events in the 220 Channel

A single 219 event will open the 220 window after a 10 msec delay. No count is recorded in the 220 window from a single event because the 215 decay will have occurred during the delay.

However, if two 219 events occur within the time constant of the 220 window opening, i.e. within 600 msec of each other, they will register. The first 219 event will open the window and the second 219 event will record, as will its coincident 215 event. Thus, 2 counts will be recorded for 219 events that occ within 600 msec. of each other.

The correction for this takes the form of equation (2) with x being the 219 count rate and t_g being 600 msec. Because the detector is not 100% efficient the probability of detecting the decay of 215 after a 219 event in the cell is cell efficiency times cpm 219.

$$\text{219 correction} = \frac{(1.6 \text{ cpm } 219)^2 t_g}{1 + (1.6 \text{ cpm } 219) t_g} \qquad (7)$$

The 1.6 factor arises because there are 2 events, each with an 80% chance of being recorded.

What is Efficiency?

Total cell efficiency (CE) is the probability of recording a count from an alpha decay within the counting cell. This is usually 0.8 to 0.9.

Total System efficiency (SE) is the the probability of recording a count from an alpha decay within the system (cell, column, tubing, pump). Here you must consider that some decays occur outside the cell. If the ratio of the cell volume to the total system volume is 0.8, the total system efficiency for a cell efficiency of 0.85 is 0.68.

Apparent System Efficiency-There are two alpha particles released for each radon decay. The apparent efficiency is the probability of detecting either of these alpha's. A system with a SE of 0.68 will have an apparent efficiency in the Total channel of 2 x

What is Efficiency?

The efficiency of the 220 channel (SE_{220}) is the probability of recording a count in the 220 channel from a ^{224}Ra decay on the fiber. Here you must consider that the probability of detecting the 220-216 coincident event is the square of the cell efficiency times the ratio of the cell volume to the total system volume. In the above example this would be 0.85 x 0.85 x 0.80 = 0.58. This is about the maximum efficiency of any RaDeCC system. Actual systems usually start with 0.50 to 0.55 efficiencies.

What is Efficiency?

The efficiency of the 219 system (SE_{219}) may differ from the 220 channel because of the differences in half live of the daughters.

1. The ^{223}Ra efficiency should be slightly less than the efficiency of^{224}Ra because the 4 sec half life of ^{219}Rn results in some decays taking place before the gas moves from the fiber column to the cell.

2. About half the ^{219}Rn decays during the first pass through the counting cell, but only ~5 % of the ^{220}Rn decays during the first pass. Thus the dead volume in the system between the counting cell and the Mn-fiber will only dilute the ^{219}Rn by 50%, but will dilute ^{220}Rn by 95%.

What is Efficiency?

3. As Rn escapes from the Mn-fiber it may follow a slow, torturous path before escaping to the air stream. This will cause more decay of ^{219}Rn than ^{220}Rn.

Measurement Errors – Some degree of uncertainty or error accompanies every analytical measurement. The major errors result from statistical variations in the decay of a limited number of atoms, the calibration of the instrument, and failure to obtain a representative sample.

Statistical variations are easy to evaluate. These are based on the number of events that are recorded in a given time period. 200 x the square root of the number of events measured divided by the number of events measured is the estimated error; in 95% of the cases the error will be within these limits

% error (95 percentile) = 200 x (square root N)/N

For example

if 100 counts are measured in 10 minutes, the estimated error is 20%, i.e. the result will fall between 80 and 120 cpm 95% of the time;

if 1000 counts are measured in 100 mins,, the estimated error is 6.3%, i.e. the result will fall between 93.7 and 106.3 cpm 95% of the time;

if 10000 counts are measured in 1000 mins., the estimated error is 2.0%, i.e. the result will fall between 98 and 102 cpm 95% of the time.