Demonstration of Capability

Method: EPA 904.0

SOPs: Ra228-Prep01, Ra228-AN01

Prep Analyst: John Doe

Prep. Analyst Signature: John Doe

Instrument Analyst: John Doe

Inst. Analyst Signature: John Doe

Matrix: Drinking Water

Units: pCi/L

Reviewed by: Jane Roe

Date of Study: 3/6/2019

QA Dept. Approval: Alma Joe

Instrument: Protean GFPC

Parameter	PQL	DOC Spike	MB1 Result	MB2 Result	MB3 Result	MB4 Result	LCS1	LCS2	LCS3	LCS4	%Rec #1	%Rec #2	%Rec #3	%Rec #4	Avg %Rec	Std. Dev.	% Rec Limits		Std. Dev. Limit
Ra-228	1	4.7	0.13	-0.02	0.26	0.23	3.9	4.1	4.6	4.4	83.12	86.21	98.90	92.79	90.26	7.03	80	120	20

Comments: **Combined radium MCL = 5 pCi/L. LCS spike levels are correctly between the DL (1 pCi/L) and MCL (5 pCi/L). LCS recoveries are all within the correct limits (80-120%)**

On the following pages, sections of the data package have been pulled out and the pertinent data for sample LCS1 is highlighted. All the appropriate calculations for sample LCS1 are shown.

Yield Determinations

Barium Sulfate
Barium Carrier ID: DL18-1265
Barium Carrier Concentration (mg/mL): 17.917 mg/mL

Barium Carrier Added (ml): 2 mL
Theoretical $BaSO_4$ Yield (mg): 60.90 mg

Comments: This method requires determination of two separate yields – barium sulfate for Ra-228 and yttrium oxalate for Ac-228. The combined yield is used in all the calculations. Also, this lab like many others, weighs the sample aliquot then converts it to a volume (e.g., for LCS1, the aliquot weighs 801.91 g. Assuming a density of 1.00 g/mL, this equates to an 801.91 mL (0.80191 L) volume.

Sample ID	Tare Weight (g)	Gross Weight (g)	Net weight (mg)	%Recovery
MB1	7.76446	7.82471	60.25	98.93%
MB2	7.73687	7.79780	60.93	100.05%
MB3	7.73252	7.79387	61.35	100.74%
MB4	7.74371	7.80348	59.77	98.14%
LCS1	7.77378	7.83562	61.84	101.54%
LCS2	7.76337	7.82357	60.20	98.85%
LCS3	7.73590	7.79663	60.73	99.72%
LCS4	7.73933	7.79827	58.94	96.78%

Sample ID	Collection Date	**Sample Aliquot (calculations)**	Sample Aliquot (measured)	**% Ba Yield** (30-110%)	$Y_2(C_2O_4)_3$ Tare (g)	$Y_2(C_2O_4)_3$ Gross (g)	$Y_2(C_2O_4)_3$ ppt (mg)	$Y_2(C_2O_4)_3$ expected (mg)	**% Yttrium Yield** (30-110%)	% Overall Yield (30-100%)
MB1	2/26/19 12:36	0.81746	817.46	98.93%	7.74234	7.76434	22.00	26.42	83.27%	82.38%
MB2	2/26/19 12:36	0.80726	807.26	100.05%	7.75064	7.77251	21.87	26.42	82.78%	82.82%
MB3	2/26/19 12:36	0.80856	808.56	100.74%	7.74180	7.76301	21.21	26.42	80.28%	80.87%
MB4	2/26/19 12:36	0.80314	803.14	98.14%	7.73164	7.75385	22.21	26.42	84.07%	82.51%
LCS1	2/26/19 12:36	0.80191	801.91	101.54%	7.75051	7.77245	21.94	26.42	83.04%	84.32%
LCS2	2/26/19 12:36	0.80184	801.84	98.85%	7.81191	7.83324	21.33	26.42	80.73%	79.81%
LCS3	2/26/19 12:36	0.80909	809.09	99.72%	7.73816	7.76017	22.01	26.42	83.31%	83.08%
LCS4	2/26/19 12:36	0.81646	816.46	96.78%	7.71047	7.73201	21.54	26.42	81.53%	78.91%

For Calculations, look at the Ba yield and Y yield data for LCS1:

Sample ID	Collection Date	Sample Aliquot (calculations)	Sample Aliquot (measured)	**% Ba Yield** (30-110%)	$Y_2(C_2O_4)_3$ Tare (g)	$Y_2(C_2O_4)_3$ Gross (g)	$Y_2(C_2O_4)_3$ ppt (mg)	$Y_2(C_2O_4)_3$ expected (mg)	**% Yttrium Yield** (30-110%)	% Overall Yield (30-100%)
LCS1	2/26/19 12:36	0.80191	801.91	101.54%	7.75051	7.77245	21.94	26.42	83.04%	84.32%

Y^{3+} in the final precipitate is based on total Y^{3+} added: 1 mL (9 mg/mL) carrier + 1 mL (0.9 mg/mL) mixed carrier = 9.9 mg Y^{3+}

$$9.9\ mg\ Y^{3+}\left(\frac{mmole\ Y_2O_3}{225.82\ mg\ Y_2O_3}\right)\left(\frac{mmole\ Y_2(C_2O_4)_3\cdot 9H_2O}{mmole\ Y_2O_3}\right)\left(\frac{603.81\ mg}{mmole\ Y_2(C_2O_4)_3\cdot 9H_2O}\right) = 26.47\ mg\ mmole\ Y_2(C_2O_4)_3\cdot 9H_2O$$

For LCS1, the yttrium oxalate precipitate recovered is 21.94 mg

$$LCS1\ (Y_2(C_2O_4)_3\cdot 9H_2O)\%\ Recovery: \frac{21.94\ mg}{26.42\ mg}\times 100 = 83.04\%$$

The *Combined Yield* of barium sulfate and yttrium oxalate must be used in all the calculations (activity, uncertainty, sensitivity):

LCS1 Combined Yield: Ba Yield x Y Yield = 1.0154 x 0.8304 = 0.8432 x 100 = 84.32%

A few additional parameters are needed to perform the calculations:

LCS1 was measured on Detector 66. Efficiency for Detector 66 = 0.4854 (see detector efficiency reported in the last column of the table on page 7)

Ac-228 decay constant (λ) = 0.113 hr^{-1} (always make sure the units in the decay constant match the time units in the calculation)

Ra-228 decay constant (λ) = 0.693/5.75 yr = 0.120 yr^{-1}

Sample ID	Start of Ac-228 Ingrowth (Date-Time) [t_1]	Start of Ac-228 Decay (Date-Time) [t_2]	Count Start (Date-Time) [t_3]	Count Duration (Min) [t_s]	Bkg Count Duration (Min) [t_B]	Ac-228 Ingrowth Time (Hours)	Ac-228 Ingrowth Factor (III)	Ac-228 Decay Time (Hours)	Ac-228 Decay Factor (Separation to Count) (I)	Ac-228 Decay Factor (during count) (II)	Ra-228 Decay Time (Years)	Ra-228 Decay Factor (Collection to Count) (IV)
MB1	2/27 @ 13:31	3/6 @ 12:10	3/6 @ 16:00	180	1000	166.7	1.000	3.84	0.6481	1.179	0.0223	0.9973
MB2	2/27 @ 13:31	3/6 @ 12:10	3/6 @ 16:00	180	1000	166.7	1.000	3.84	0.6476	1.179	0.0223	0.9973
MB3	2/27 @ 13:31	3/6 @ 12:10	3/6 @ 16:00	180	1000	166.7	1.000	3.84	0.6474	1.179	0.0223	0.9973
MB4	2/27 @ 13:31	3/6 @ 12:10	3/6 @ 16:00	180	1000	166.7	1.000	3.84	0.6474	1.179	0.0223	0.9973
LCS1	2/27 @ 13:31	3/6 @ 12:10	3/6 @ 16:00	180	1000	166.7	1.000	3.84	0.6480	1.179	0.0223	0.9973
LCS2	2/27 @ 13:31	3/6 @ 12:10	3/6 @ 16:00	180	1000	166.7	1.000	3.84	0.6478	1.179	0.0223	0.9973
LCS3	2/27 @ 13:31	3/6 @ 12:10	3/6 @ 16:00	180	1000	166.7	1.000	3.84	0.6473	1.179	0.0223	0.9973
LCS4	2/27 @ 13:31	3/6 @ 12:10	3/6 @ 16:00	180	1000	166.7	1.000	3.84	0.6477	1.179	0.0223	0.9973

There are four decay and ingrowth factors that are calculated and incorporated into activity, uncertainty and sensitivity determinations. Verify the factors shown in the above table:

(I) **Calculate Ac-228 decay factor from separation to start of count (column 10)**:

$$\mathrm{I} = e^{-\lambda_{Ac228}(t_3 - t_2)}$$

Substituting the values for the Ac-228 decay constant (λ = 0.113 hr^{-1}) and $t_3 - t_2$ (3.84 hours – you don't have to hand calculate this, the computer program has already done it for you in column 9):

$$\mathrm{I} = e^{(-0.113\ hr^{-1})(3.84\ hr)}$$

$$\mathrm{I} = 0.6480$$ √

(II) **Calculate Ac-228 decay factor for decay during the count (column 11) - note sample count time was 180 minutes = 3 hours**:

$$\mathrm{II} = \frac{\lambda_{Ac228} t_s}{1 - e^{-\lambda_{Ac228} t_s}}$$

$$\mathrm{II} = \frac{(0.113\ hr^{-1})(3\ hr)}{1 - \left(e^{(-0.113\ hr^{-1})(3\ hr)}\right)}$$

$$\mathrm{II} = 1.179$$ √

(III) **Calculate Ac-228 ingrowth factor from the start of ingrowth to the time of separation (column 8)**:
A minimum 36-hour ingrowth time is specified in the method. At 36 hours, ingrowth is about 98%. Longer ingrowth time makes this factor negligible in the calculations.

$$\mathrm{III} = 1 - e^{-\lambda_{Ac228}(t_2 - t_1)}$$

$$\mathrm{III} = 1 - e^{(-0.113\ hr^{-1})(166.7\ hr)}$$

$$\mathrm{III} = 1 - (6.6 \times 10^{-10})$$

$$\mathrm{III} = 1.0$$ √

(IV) **Calculate Ra-228 decay from time of collection (last column)**. Some caveats: If samples are received and analyzed within a couple of weeks, the contribution associated with Ra-228 decay is negligible and often not accounted for in the calculations (half-life is 5.75 years as compared to the half-life of Ac-228 which is 6.15 hours). There are two commonly accepted ways for calculating the Ra-228 decay factor and, as shown in the calculations that follow, both yield equivalent results.

(A) Calculate the Ra-228 decay factor from the time of collection until the end of the count time: Looking at the data package, the samples were collected on 2/26 at 12:36. Sample count was started on 3/6 at 16:00. The count duration was 180 minutes. Fortunately, instrument software is configured to compile the time. But if you work from beginning to end, the total time from collection to the end of the sample count is 8 days, 5 hours and 24 minutes. That is a total of 200.4 hours. Since the Ra-228 half-life is in years, convert 200.4 hours into years: 0.0228767 year.

$$\mathrm{IV} = e^{-\lambda_{Ra228}(t_3 - t_0 + t_s)}$$

$$\mathrm{IV} = e^{(-0.120\ yr^{-1})(0.0228767\ yr)}$$

$$\mathrm{IV} = 0.9973$$ √

(B) Calculate the Ra-228 decay factor from the time of collection until the start of Ac-228 decay. Again, samples were collected on 1/26 at 12:36. Start of Ac-228 decay begins on 3/6 at 12:10. The total time is 7 days, 23 hours and 26 minutes. That is a total of 191.43 hours. Converting to years: 0.02185 year.

$$\mathrm{IV} = e^{-\lambda_{Ra228}(t_2 - t_0)}$$

$$\mathrm{IV} = e^{-0.120\ yr^{-1}(0.02185\ yr)}$$

$$\mathrm{IV} = 0.9974$$ √

Calculate Ra-228 Activity for LCS1 in pCi/L

Sample ID	Ra-228 Activity (pCi/L)	Two-sigma Counting Uncertainty	MDC	Detector ID	Beta Gross Counts per Minute (cpm)	Beta Background Counts per Minute (cpm)	Activity Conversion Factor	Ac-228 (Sr-89) Efficiency
MB1	0.130	0.233	0.513	65	0.3444	0.2930	2.22	0.4818
MB2	-0.020	0.220	0.523	71	0.3000	0.3080	2.22	0.4880
MB3	0.256	0.232	0.474	72	0.3278	0.2300	2.22	0.4806
MB4	0.231	0.233	0.483	73	0.3389	0.2490	2.22	0.4831
LCS1	3.905	0.519	0.576	66	1.9444	0.3850	2.22	0.4854
LCS2	4.050	0.536	0.577	68	1.8889	0.3480	2.22	0.4888
LCS3	4.646	0.555	0.564	74	2.2056	0.3630	2.22	0.4855
LCS4	4.359	0.545	0.543	69	1.9722	0.3080	2.22	0.4872

$$A = \frac{Net\ Count\ Rate, R_N}{2.22 \times E \times V \times Y_{Combined}} \times \frac{\lambda_{Ac228} t_s}{(1 - e^{-\lambda_{Ac228} t_s})} \times \frac{1}{(1 - e^{-\lambda_{Ac228}(t_2 - t_1)})} \times \frac{1}{e^{-\lambda_{Ac228}(t_3 - t_2)}} \times \frac{1}{e^{-\lambda_{Ra228}(t_3 - t_0 + t_s)}}$$

Parameters for LCS1:

Net Count Rate = Beta Gross cpm – Beta Background cpm (columns 6 and 7 on this page)

2.22 = conversion factor, count rate to pCi

E = efficiency for detector 66 = 0.4854 (last column on this page). As noted, Sr-89 is used as the calibrant for detector efficiency determination

V = sample aliquot volume, L = 0.8019 (column 2 on page 2)

$Y_{Combined}$ = combined barium and yttrium yields = 0.8432 (combined yield calculation on page 3)

Ingrowth and decay factors as calculated on pages 4 and 5:

$\frac{\lambda_{Ac228} t_s}{(1 - e^{-\lambda_{Ac228} t_s})}$ = 1.179

$1 - e^{-\lambda_{Ac228}(t_2 - t_1)}$ = 1.0

$e^{-\lambda_{Ac228}(t_3 - t_2)}$ = 0.6480

$e^{-\lambda_{Ra228}(t_3 - t_0 + t_s)}$ = 0.9973

$$A = \frac{1.9444\ cpm - 0.3850\ cpm}{2.22(0.4854)(0.8019\ L)(0.8432)} \times 1.179 \times \frac{1}{1.0} \times \frac{1}{0.6480} \times \frac{1}{0.9973} = 3.904 \frac{pCi}{L}$$

Calculate Counting Uncertainty for LCS1:

$$u_c = \frac{\sqrt{\frac{R_s}{t_s} + \frac{R_b}{t_b}}}{2.22 \times E \times V \times Y_{Combined}} \times \frac{\lambda_{Ac228} t_s}{(1 - e^{-\lambda_{Ac228} t_s})} \times \frac{1}{(1 - e^{-\lambda_{Ac228}(t_2 - t_1)})} \times \frac{1}{e^{-\lambda_{Ac228}(t_3 - t_2)}} \times \frac{1}{e^{-\lambda_{Ra228}(t_3 - t_0 + t_s)}}$$

Parameters for LCS1:
Sample count rate, R_s = 1.9444 cpm
Background count rate, R_b = 0.3850 cpm
Sample count time, t_s =180 min
Background count time, t_b =1000 min
2.22 = conversion factor, count rate to pCi

E = efficiency for detector 66 = 0.4854 (last column on page 7)

V = sample aliquot volume, L = 0.8019 (column 2 on page 2)

$Y_{Combined}$ = combined barium and yttrium yields = 0.8432 (combined yield calculation on page 3)

Ingrowth and decay factors as calculated on pages 4 and 5:

$\frac{\lambda_{Ac228} t_s}{(1 - e^{-\lambda_{Ac228} t_s})}$ = 1.179

$1 - e^{-\lambda_{Ac228}(t_2 - t_1)}$ = 1.0

$e^{-\lambda_{Ac228}(t_3 - t_2)}$ = 0.6480

$e^{-\lambda_{Ra228}(t_3 - t_0 + t_s)}$ = 0.9973

$$u_c = \frac{\sqrt{\frac{1.9444\ cpm}{180\ min} + \frac{0.3850\ cpm}{1000\ min}}}{2.22(0.4854)(0.8019\ L)(0.8432)} \times 1.179 \times \frac{1}{1.0} \times \frac{1}{0.6480} \times \frac{1}{0.9973} = 0.2645$$

Report the 2-sigma counting uncertainty (see column 3 on page 7): Remember, even though we say ‘2-sigma’, the statistical multiplier is 1.96, not 2.

$$2\sigma = 1.96 u_c = 0.519$$

Verify the MDC for LCS1:

$$MDC = \frac{\frac{2.71}{t_s} + \left(4.65\sqrt{\frac{R_b}{t_s}}\right)}{2.22 \times E \times V \times Y_{Combined}} \times \frac{\lambda_{Ac228} t_s}{(1 - e^{-\lambda_{Ac228} t_s})} \times \frac{1}{(1 - e^{-\lambda_{Ac228}(t_2 - t_1)})} \times \frac{1}{e^{-\lambda_{Ac228}(t_3 - t_2)}} \times \frac{1}{e^{-\lambda_{Ra228}(t_3 - t_0 + t_s)}}$$

Parameters for LCS1:

Background count rate, R_b = 0.3850 cpm

Sample count time, t_s =180 min

2.22 = conversion factor, count rate to pCi

E = efficiency for detector 66 = 0.4854 (last column on page 7)

V = sample aliquot volume, L = 0.8019 (column 2 on page 2)

$Y_{Combined}$ = combined barium and yttrium yields = 0.8432 (combined yield calculation on page 3)

Ingrowth and decay factors as calculated on pages 4 and 5:

$\frac{\lambda_{Ac228} t_s}{(1-e^{-\lambda_{Ac228} t_s})}$ = 1.179

$1 - e^{-\lambda_{Ac228}(t_2 - t_1)}$ = 1.0

$e^{-\lambda_{Ac228}(t_3 - t_2)}$ = 0.6480

$e^{-\lambda_{Ra228}(t_3 - t_0 + t_s)}$ = 0.9973

$$MDC = \frac{\frac{2.71}{180} + \left(4.65\sqrt{\frac{0.3850}{180}}\right)}{2.22(0.4854)(0.8019\ L)(0.8432)} \times 1.179 \times \frac{1}{1.0} \times \frac{1}{0.6480} \times \frac{1}{0.9973} = 0.576$$

***The calculated activity, 2-sigma counting uncertainty and MDC agree with the values provided in the data package shown on page 7**.

For drinking water samples, determine the SDWA detection limit for LCS1 using the same parameters described above:

$$SDWA\ DL = \frac{\frac{1.96^2}{2t_s}\left[1 + \sqrt{1 + \left(\frac{4t_s^2}{1.96^2} \times R_b \times \left(\frac{1}{t_s} + \frac{1}{t_b}\right)\right)}\right]}{2.22 \times E \times V \times Y_{Combined}} \times \frac{\lambda_{Ac228} t_s}{\left(1 - e^{-\lambda_{Ac228} t_s}\right)} \times \frac{1}{\left(1 - e^{-\lambda_{Ac228}(t_2 - t_1)}\right)} \times \frac{1}{e^{-\lambda_{Ac228}(t_3 - t_2)}} \times \frac{1}{e^{-\lambda_{Ra228}(t_3 - t_0 + t_s)}}$$

$$SDWA\ DL = \frac{\frac{3.8416}{2(180)}\left[1 + \sqrt{1 + \left(\frac{4(180^2)}{3.8416} \times 0.3850 \times \left(\frac{1}{180} + \frac{1}{1000}\right)\right)}\right]}{2.22(0.4854)(0.8019\ L)(0.8432)} \times 1.179 \times \frac{1}{1.0} \times \frac{1}{0.6480} \times \frac{1}{0.9973} = 0.275$$

0.275 < Ra-228 regulatory DL (1.0)