Gross Alpha Analytical Modifications that Improve Wastewater Treatment Compliance

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ABSTRACT

This paper will propose an improvement to the gross alpha measurement that will provide more accurate gross alpha determinations and thus allow for more efficient and cost-effective treatment of site wastewaters.

To evaluate the influence of salts that may be present in wastewater samples from a potentially broad range of environmental conditions, two types of efficiency curves were developed, each using a thorium-230 (Th-230) standard spike. Two different aqueous salt solutions were evaluated, one using sodium chloride, and one using salts from tap water drawn from the Bergen County, New Jersey Publicly Owned Treatment Works (POTW). For each curve, 13 to 17 solutions were prepared, each with the same concentration of Th-230 spike, but differing in the total amount of salt in the range of 0 to 100 mg. The attenuation coefficients were evaluated for the two salt types by plotting the natural log of the counted efficiencies vs. the weight of the sample's dried residue retained on the planchet. The results show that the range of the slopes for each of the attenuation curves varied by approximately a factor of 2.5.

In order to better ensure the accuracy of results, and thus verify compliance with the gross alpha wastewater effluent criterion, projects depending on gross alpha measurements of environmental waters and wastewaters should employ gross alpha efficiency curves prepared with salts that mimic, as closely as possible, the salt content of the aqueous environmental matrix.

INTRODUCTION

Radiologically contaminated sites are often faced with the challenge of treating wastewater obtained during excavation of contaminated soils, and collected from runoff of stormwater that was in contact with contaminated soil. The treatment process strategy depends on the activities of radionuclides in the water. The water must be tested for various radioisotopes as well as gross alpha and gross beta.

The gross alpha test results are often used to determine the acceptability for discharge of groundwaters and surface waters suspected of being radiologically contaminated. An acceptance

criterion, or maximum contaminant level (MCL), has been established in accordance with the National Interim Primary Drinking Water Regulations [1]. This criterion states that the gross alpha activity, excluding radon and uranium, must be less than 15 pCi/L.

This paper will focus on the gross alpha measurement. It will show that efficiency curves generated as part of the gross alpha measurement procedure should be prepared using solutions that mimic the salt content of site waters to the greatest extent practicable.

DISCUSSION

A gross alpha activity measurement using a gas proportional detector employs an attenuation or efficiency curve [2]. The attenuation curve estimates the efficiency of detection of alpha particles based upon the thickness of solid salt residue on a sample planchet following evaporation of an aqueous sample suspected of containing dissolved or suspended alpha particle emitting salts. Some percentage of the alpha particles being released from a radionuclide spiked into the residue are self-adsorbed. This self-adsorption or attenuation is a function of the sample's composition and geometry, namely its average atomic number, density, thickness, as well as the energy of the alpha particles. The attenuation curve is subsequently used to calculate gross alpha activity based upon the weight of solid residue remaining following evaporation of a water sample. Water sample activities are significantly influenced by the type and concentration of salt(s) used to generate the efficiency curve.

Efficiency curves were prepared from two sets of salt solutions as follows:

Set 1: Eight curves corresponding to eight detectors each using 17 evaporated sodium chloride solution residues ranging in weight from approximately 0 to 100 milligrams (mg)
Set 2 : Sixteen curves corresponding to sixteen detectors each using 13 evaporated tap water residues ranging in weight from approximately 0 to 100 milligrams (mg)

Both Sets 1 and 2 were generated in the USACE FUSRAP Maywood Laboratory (UFML) in Maywood, NJ. Details of the procedure are provided below.

EQUIPMENT

1. Multi-Detector Gas Proportional Detection System (MDS), Model MPC 9604; Protean Instrument Corporation; software - Protean MDS Control Panel® Version 1.3
2. Plastic sample carriers to include snap in adapters to accommodate two inch diameter samples 5/16 inches deep; Protean Instrument Corp
3. Planchets 2 inches in diameter and 5/16 inches deep, Protean Instrument Corp.
4. Two stage gas pressure regulator, non-flammable gas, left-hand threading; Protean Instrument Corp.
5. Thermolyne Cimarec 3 12X12 Hot Plate 0 – 250ºC, minimum

REAGENTS

1. NIST traceable calibration standard Th-230, 3000-5000 dpm; Analytics Inc.

2. P-10 gas, Class A cylinder, 2500 psig; SOS Gas Co.

3. Nitric Acid, Fisher Scientific 50-70% Certified ACS Plus

PROCEDURE

For Set 1, seventeen volumes of sodium chloride solution were each spiked with 253 pCi of Th-230 (5 mls of 50.54 pCi/ml Th-230) Each sample varied the volume of salt solution depending upon the desired weight of residue.   The volumes and final residue weights are shown in Table 1 below. For Set 2, thirteen volumes of tap water in 600 ml beakers were each spiked with 758 pCi of Th-230 (15 mls of 50.54 pCi/ml Th-230). The samples in both Sets were prepared in accordance with EPA Method 900.0 [2]. The beakers were placed on hot plates, and the solutions were heated and evaporated to a small volume of approximately 5 mls. Concentrated nitric acid is then added in two 5 ml portions, and the solution is heated to near dryness. Ten milliliters of 1M HNO_3 is then added to dissolve the residue and the solution is transferred quantitatively to a tared planchet. The planchet solution was evaporated to dryness on the hotplate. The planchet was then cooled in a desiccator. After cooling, the planchet was transferred to the counting room for counting. Sets 1 and 2 samples were counted on a Protean MDS Model MPC 9604 for 145 and 45 minutes, respectively.

Table I.   Volumes of Salt Solutions and Corresponding Residue Weights

Aliquot No.	Set 1		Set 2	
	Volume (mls)	Residue Weight (mg)	Volume (mls)	Residue Weight (mg)
1	0	0.00	0	0
2	1.5	3.10	2	0.5
3	3	6.60	10	4.8
4	4.5	9.40	20	11
5	6	10.60	30	16.7
6	9	15.70	50	27.5
7	12	28.70	75	41.6
8	15	31.40	100	53.1
9	18	39.00	115	57.6
10	22	46.90	125	67.6
11	26	47.60	145	73.9
12	30	61.40	170	86.5
13	34	70.00	200	99.8
14	38	76.00		
15	42	85.80		
16	46	91.20		
17	50	96.50		

CALCULATIONS

The efficiency of detection of alpha particles is affected by the degree of attenuation of the alpha particles within the salt, the ionization efficiency of the argon/methane gas, and the detector efficiency. The overall efficiency is expressed as:

Efficiency $=$ C / A$_{std}$ $\hspace{8cm}$ (Eq. 1)

Where C = the net signal obtained in counts per minute
$\hspace{1cm}$ A$_{std}$ = the activity of the Th-230 standard added in dpm

The calculated efficiencies, as well as the natural log (ln) of the efficiencies were plotted against the residue weights to determine if a useful mathematical relationship existed. A linear regression analysis was performed to see if the relationship was linear. The regression coefficients were closer to one for the ln (efficiency) versus weight, ranging from between 0.97 to 0.98 for Set 1, and all approximately 0.98 for Set 2. Therefore, the mathematical relationship between ln(efficiency) and weight of residue was used for this paper.

The slope, intercept and correlation coefficient of the linear regression calculated for each detector is provided in Table 2 below. The average slope between the two Sets varies by about a factor of 2.4. The correlation coefficients of 0.97 to 0.98 indicate a fair degree of linearity. The precision of the detectors within the MDS is very good, as shown by the low relative standard deviation ((average/std. deviation) X 100) of the curve slopes, 1.5% for Set 1 and 2.9% for Set 2.

When one calculates the gross alpha activity of a sample that has been tested using a gas proportional detector, the efficiency is used in the calculation and the efficiency value is taken from an efficiency curve such as those that we have plotted in this paper.

Activity, (pCi/l) $=$ C / (E)(V) 2.22 $\hspace{7cm}$ (Eq. 2)

Where C = net counts per minute (cpm; net is gross cpm – background cpm) obtained from the sample measurement
$\hspace{1cm}$ E = overall efficiency, obtained from the plotted curve
$\hspace{1cm}$ V = volume of sample
$\hspace{1cm}$ 2.22 = conversion factor from disintegrations per minute (dpm) to pCi

For a given wastewater sample volume of 0.2 liter that yields a residue of 50 mg following sample preparation/evaporation, the efficiency calculated using the average slope and intercept from Sets 1 and 2 are as follows:

Set 1

Ln(Efficiency) $=$ -0.004415 (50 mg) - 1.331
Ln(Efficiency) $=$ -1.55
Efficiency $=$ 0.21

Table II. Linear Regression Indicators for Detectors in Sets 1 and 2

SET 1 - Sodium Chloride Salt Solutions			
Detector	**Slope**	**Intercept**	**Correlation Coefficient**
P1A	-0.004414	-1.355	-0.981
P1B	-0.004466	-1.33	-0.977
P1C	-0.004479	-1.325	-0.973
P1D	-0.004456	-1.328	-0.969
P2A	-0.00447	-1.318	-0.971
P2B	-0.004323	-1.327	-0.975
P2C	-0.004307	-1.322	-0.975
P2D	-0.004402	-1.34	-0.97
Average:	**-0.00441**	**-1.331**	**-0.974**
Standard Deviation:	**0.0000673**	**0.0118**	**0.00398**
SET 2 - Tap Water			
Detector	**Slope**	**Intercept**	**Corr. Coefficient**
P1A	-0.01091	-1.43	-0.979
P1B	-0.0109	-1.424	-0.978
P1C	-0.01082	-1.432	-0.978
P1D	-0.01076	-1.431	-0.974
P2A	-0.01083	-1.418	-0.981
P2B	-0.0106	-1.414	-0.977
P2C	-0.01058	-1.419	-0.977
P2D	-0.01095	-1.432	-0.976
P3A	-0.01022	-1.453	-0.982
P3B	-0.01037	-1.454	-0.984
P3C	-0.01035	-1.461	-0.983
P3D	-0.01018	-1.462	-0.983
P4A	-0.01021	-1.451	-0.982
P4B	-0.01028	-1.453	-0.982
P4C	-0.01008	-1.453	-0.98
P4D	-0.01029	-1.478	-0.984
Average:	**-0.0105**	**-1.442**	**-0.980**
Standard Deviation:	**0.000305**	**0.0188**	**0.00308**

Set 2

Ln(Efficiency) = -0.01052 (50 mg) - 1.442
Ln(Efficiency) = -1.55
Efficiency = 0.14

This calculation shows that the Set 1 efficiency 50% greater than the Set 2 efficiency for a 50 mg residue. This variability will change with the mass of residue. An 80 mg residue will yield efficiencies of 0.19 and 0.10, respectively for Set 1 and Set 2.

For the 50 mg test case, using a C value of 1.0 cpm and Equation 2, activities of 10.7 pCi./l for Set 1, and 16.1 pCi/l for Set 2 are calculated as shown below.

Set 1

Activity, (pCi/l) = 1.0 cpm / (0.21 cpm/dpm)(0.2 liter) (2.22 dpm/pCi)
Activity, (pCi/l) = 10.7 pCi/l

 Set 2

Activity, (pCi/l) = 1.0 cpm / (0.14 cpm/dpm)(0.2 liter) (2.22 dpm/pCi)
Activity, (pCi/l) = 16.1 pCi/l

CONCLUSION

Since the activity of a wastewater sample is inversely proportional to the detector efficiency, these results show that the calculated activity can vary by a factor of up to two, depending upon the type of salt solution employed in the preparation of the efficiency curve.

This calculation illustrates the importance of choosing and constructing the appropriate efficiency curve. In the hypothetical example above, if the Set 1 efficiency curve were chosen, the activity would be 10.7 pCi/l, which is less than the regulatory action level or maximum contaminant level (MCL) of 15 pCi/l. If the Set 2 efficiency curve were chosen, the activity would be 16.1 pCi/l, which is greater than the regulatory action level.   The composition of the salt solution selected for construction of an efficiency curve to be used for gross alpha measurement using a gas proportional detector is critical to the accuracy of the calculated sample activities. The salt solution should mimic, to the best extent possible, the dissolved salt content of the wastewater samples that will be analyzed. If a curve is constructed that yields an efficiency that is lower than the true efficiency, the calculated activity will be biased high. Such high bias may cause the activity to be falsely above regulatory action levels, and trigger costly and unnecessary treatment of the wastewater.

Additional investigation of mixed salt residues, preferably ones that mimic the salt signature of some groundwaters or wastewaters, will be pursued to gain a better understanding of the

variability in the emanation rates of alpha particles from salts and gas proportional detection efficiencies.

REFERENCES

1. U.S. Environmental Protection Agency, National Interim Primary Drinking Water Regulations, Federal Register: December 16, 1998 (Volume 63, Number 241)
2. U.S. Environmental Protection Agency, Prescribed Procedures for Measurement of Radioactivity in Drinking Water, Method 900.0, EPA-600/4-80-032, August 1980.