

# Application Note

Alpha/Beta

ABA-008

## A New Approach to Gross Alpha Measurements in Aqueous Samples Using Extraction Chromatography and Liquid Scintillation Counting

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### Abstract

A new approach to the measurement of gross alphas in liquid samples, which combines Eichrom's extraction technology with Packard's liquid scintillation analysis technology, is presented. Difficulties with sample preparation and detection efficiency have always been problematic with the traditional method of gas flow proportional counting (GPC). The use of Eichrom's extraction resins and alpha liquid scintillation counting (LCS) has resolved the sample preparation problems, associated with drying the sample on a planchet. With its superior detection efficiency over GPC, this combination provides a better counting platform. Thus, many of the inherent limitations associated with the traditional GPC method are overcome by using this new approach and results demonstrate faster sample preparation, lower detection limits and shorter counting times.

### Introduction

The traditional method of gross alpha measurements for liquid samples using GPC suffers from a number of limitations. In order to minimize the problem of self absorption, the volume of sample which can be analyzed is limited by the amount of dissolved solids found in the aqueous samples (typically environmental and process waters). Counting efficiency of alpha particles by GPC is 35% to 40% at best (0 mg residue) and declines to less than 10% when 100 mg of solids are left on the counting

planchet. Counting times in excess of 1000 minutes are typically required to reach a detection limit of 100 mBq/L. Samples containing extremely high levels of dissolved solids may require even longer counting times to achieve the desired detection limit since an even smaller sample size must be used. Alpha LSC has been proposed as an alternate to GPC for gross alpha measurements. The inherent counting efficiency for alpha particles by LSC is in excess of 90%. Since it does not suffer from self absorption problems, LSC can handle higher levels of dissolved solids. However, the sample size is limited by what can be put into an LSC vial, and so for samples larger than 10 mL, some form of sample concentration must be performed. As shown in Figures 1 and 2, Eichrom Industries actinide resin shows excellent uptake for all the actinides and for radium under neutral to slightly acidic conditions,<sup>1,2</sup> and is therefore a good candidate to preconcentrate samples prior to alpha LSC. The actinide resin (using the Dipex<sup>®</sup> extractant<sup>3</sup>) is an extraction chromatographic resin in which the functional group on the extractant molecule is a diphosphonate moiety. The structure of this molecule is shown in Figure 3.

A method has been developed which combines this resin and alpha LSC to measure total alpha activity in water samples. The method is fast and simple. As many as 20 samples can be processed in 24 hours, requiring only one to two hours of hands-on time. Using 100 mL samples, a detection limit of 2 pCi/L (75 mBq/L) can be reached with only 60 minutes counting time.



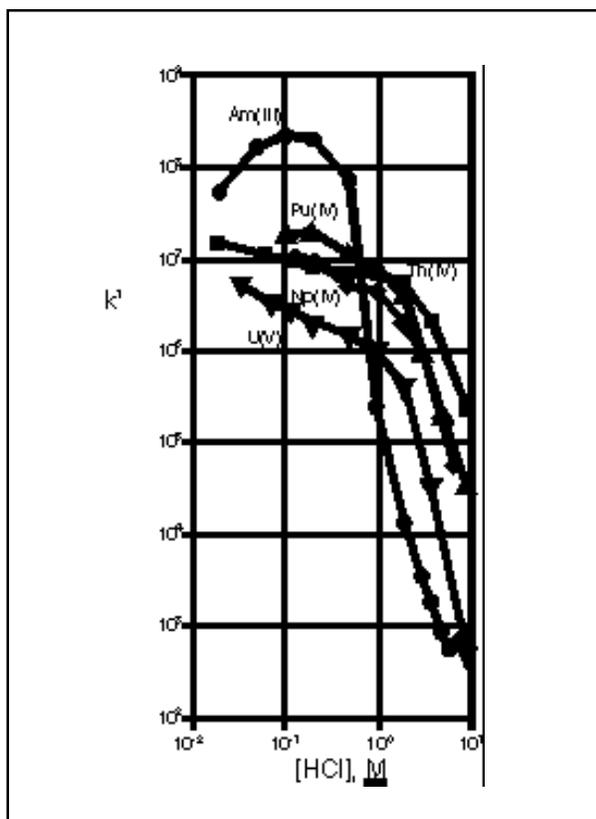
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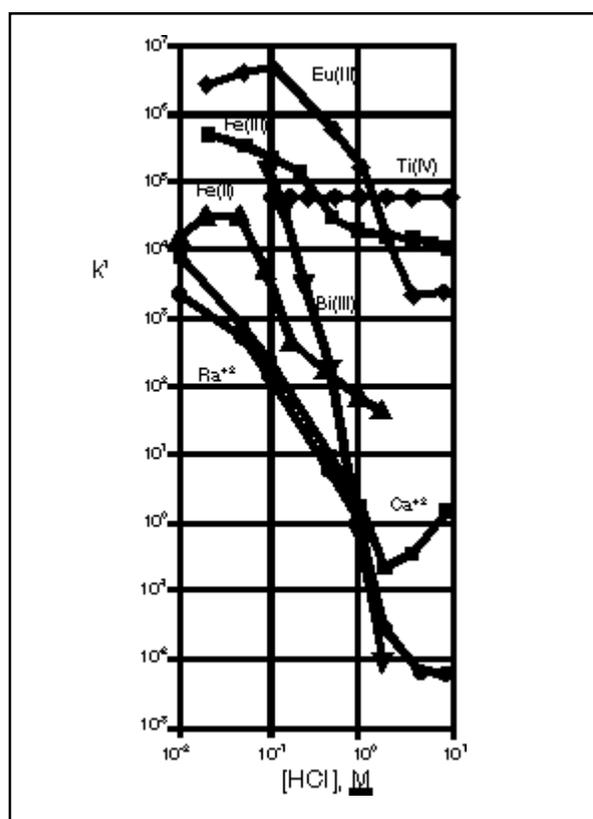
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**Figure 1.**  
Acid dependency of the uptake of several actinide species by the Dipex resin.



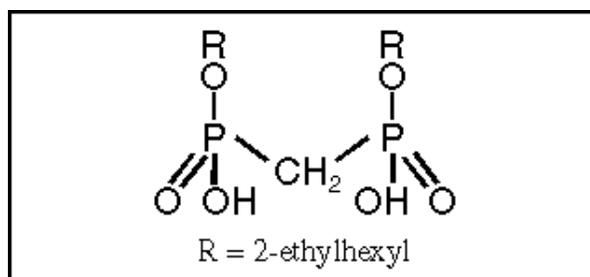
**Figure 2.**  
Acid dependency of the uptake of several non-actinide species by the Dipex resin.

## Experiment

Actinide resin (0.5 g) was added to one liter of a spiked water sample acidified to pH 2 with  $\text{HNO}_3$ , and stirred on a magnetic stir plate. After the indicated contact time, the resin was collected using a vacuum filtration apparatus and a 0.45 micron Gelman filter. The resin was rinsed with deionized (DI) water and the filter containing the collected resin was transferred to a watch glass and placed under a heat lamp (approximately 75 cm above) for approximately 15 minutes to gently dry the resin. The dried resin was carefully transferred into a glass scintillation vial and the filter rinsed with 1 mL of 0.5M HCl. The 0.5M HCl rinse was collected in the scintillation vial. Ten mL Ultima Gold LLT was added and the alpha activity was counted on a Packard Tri-Carb<sup>®</sup> 2550TR/AB liquid scintillation counter. Count times were 30 or 60 minutes as indicated and the alpha region of interest was set between 90 and 500 keV. The alpha/beta discriminator setting (124) was determined following the procedure in the instrument instruction manual, using  $^{210}\text{Po}$  as the pure alpha source and  $^{90}\text{Sr}/^{90}\text{Y}$  as the pure beta source. Vials used in the discriminator setting procedure had the same composition as the actual samples (*i.e.*, 0.5 g actinide resin, 1 mL 0.5M HCl, and 10 mL Ultima Gold LLT). Blank samples were prepared as follows: 0.5 g actinide resin, 1 mL 0.5 M HCl, and 10

mL Ultima Gold LLT were added to a glass scintillation vial. Direct spikes were prepared in the same manner as the blanks except that the appropriate spike was also added directly to the scintillation vial. The simulated ground water matrix was prepared with two stock solutions; the composition is shown in Table 1.

One liter of each stock solution was prepared with high purity water. Twenty-five mL of each stock solution was added to 900 mL of high purity water and mixed. The pH of the resulting solution was adjusted to 9.8 using 0.1M HCl and 0.1M NaOH, as necessary. The solution was then diluted to a final volume of 1000 mL. Aliquots of this solution were spiked and used in the procedure as the simulated ground water matrix.



**Figure 3.**  
Eichrom Dipex extractant.

<b>Stock A:</b>			
<b>Constituent</b>	<b>mg/L</b>	<b>Added As</b>	<b>Amount Per Liter of Stock Solution</b>
Al	0.238	Al(NO <sub>3</sub> ) <sub>3</sub>	75 mg
K	14	KCl	1.07 g
Ca	23	CaCl <sub>2</sub>	228 mL of 0.1M solution
Cl	410	2M HCl	-201 mL
<b>Stock B:</b>			
<b>Constituent</b>	<b>mg/L</b>	<b>Added As</b>	<b>Amount Per Liter of Stock Solution</b>
Si	75	Na <sub>2</sub> SiO <sub>3</sub> ·9H <sub>2</sub> O	30.36 g
Inorganic carbon	18	Na <sub>2</sub> CO <sub>3</sub>	6.35 g
F	35	NaF	3.09 g
SO <sub>4</sub>	170	Na <sub>2</sub> SO <sub>4</sub>	10.06 g
Na	360	50% NaOH	-3 grams

**Table 1.**  
Ground water composition.

## Results and Discussion

Percentage uptake of various spikes of alpha emitters of interest were measured using the procedure, previously described. <sup>241</sup>Am, <sup>234/238</sup>U, <sup>232</sup>Th and <sup>226</sup>Ra were used. The uptake of <sup>241</sup>Am and <sup>234/238</sup>U from 500 mL of DI water with a 30 minute contact time is shown in Tables 2 and 3.

Americium uptake was excellent as was expected from the theoretical behavior of <sup>241</sup>Am on the actinide resin. The uranium recoveries were not as expected. Since thermodynamically, the actinide resin should have taken up all of the uranium, we evaluated whether there was some kinetic issue related to uptake onto the resin. Correspondingly, the contact time of the sample with the actinide resin was extended. In Table 4, the uranium spike recoveries at various sample contact times are shown.

Sample	Spike (DPM)	Measured (CPM)	Measured (DPM)	Recovery (%)
Blank	---	0.50	---	---
1	13.4	12.5	13.1	97.6%
2	13.4	11.9	12.5	93.1%

**Table 2.**  
Uptake of <sup>241</sup>Am (91.6% efficiency).

Sample	Measured (CPM)	Measured (DPM)	Recovery (%)
Blank	0.73	---	---
Direct Spike	26.3	26.8	95.5%
1	9.83	9.53	35.6%
2	9.87	9.57	35.7%
3	7.97	7.58	28.3%

**Table 3.**  
Uptake of <sup>234/238</sup>U at 30 minute contact time.

Contact Time (hr)	Number Samples	Average (CPM)	Average (DPM)	Recovery (%)
0.5	3	9.22	8.89	33.2%
1	3	14.1	14.0	52.2%
4	3	26.6	27.1	101%
18	3	26.3	26.8	100%

**Table 4.**  
Effect of contact time on <sup>234/238</sup>U spike recovery.

The data indicates a relationship between contact time and uranium spike recovery. At four hours contact time, the recovery is quantitative. The 18 hour contact period represents overnight (unattended) contact of the resin with the sample. Unattended operations which can be carried out overnight are attractive to routine production laboratories because of the effective use of space and time. This contact time period was chosen for all future experiments. Based on the data in Table 4, it is expected that four hour contact time is also adequate. Spike recoveries of thorium and radium from DI water (18 hour contact time) were acceptable. See Table 5.

The one low recovery for thorium represented a sample in which there was non-quantitative transfer of the actinide resin from the filter paper to the scintillation vial. The next step in the evaluation of this procedure was to test it on samples of the simulated ground water matrix. See Tables 6 and 7.

All the actinides show good uptake from 500 mL samples. Thorium recoveries, while not quantitative, were equivalent to the recoveries observed from DI water. Radium recoveries, however, were poor (see Table 7). As might be predicted from the data in Table 7, the calcium present in the simulated ground water matrix, appears to prevent (or possibly block) the uptake of radium on the actinide resin. Subsequent experiments from 100 mL samples of the simulated matrix showed much better uptake, probably due to the lower overall level of calcium present. The results are equivalent to the DI water recoveries in Table 5. See Table 8 for these results.

The final test of the method was to analyze actual environmental samples which had been previously characterized for gross alpha activity by the traditional evaporation/GPC method. Twenty-four (24) samples were received from the United States Geological Surveys National Water Quality Lab (NWQL) in Arvada, Colorado. These samples represented ground water samples from across the United States. Total dissolved solids (TDS) content had been measured on ten of these samples, ranging as high as 1700 mg/L. Overall the results obtained for the 24 samples using the proposed LSC method agreed extremely well with those previously obtained using the GPC method. The data shown in Table 9 are the results determined by each method along with the 2 sigma total propagated uncertainty (TPU).

Sample	Net Counts (CPM)	% Direct Spike
Th-direct spike	47.6	100%
Th-1	37.4	78.6%
Th-2	36.0	75.6%
Th-3	26.5	55.7%
Ra-direct spike	58.2	100%
Ra-1	50.5	86.8%
Ra-2	43.2	74.2%
Ra-3	51.6	88.7%

**Table 5.**  
Spike recoveries with <sup>232</sup>Th and <sup>226</sup>Ra.

Sample	Measured (CPM)	Calculated (DPM)	Recovery (%)
Direct spike (53.6 DPM)	56.7	53.6	102%
Blank	1.83	---	---
1	53.4	51.6	96.2%
2	53.0	31.2	95.5%

**Table 6.**  
<sup>234/238</sup>U uptake from simulated ground water matrix.

Sample	Net Counts (CPM)	% Direct Spike
Th-direct spike	50.3	100%
Th-1	37.3	74.2%
Th-2	39.3	78.1%
Ra-direct spike	56.5	100%
Ra-1	11.2	19.8%
Ra-2	10.4	18.4%

**Table 7.**  
<sup>232</sup>Th and <sup>226</sup>Ra uptake from simulated ground water matrix.

Sample	% Recovery
Ra-1	82.7%
Ra-2	74.7%

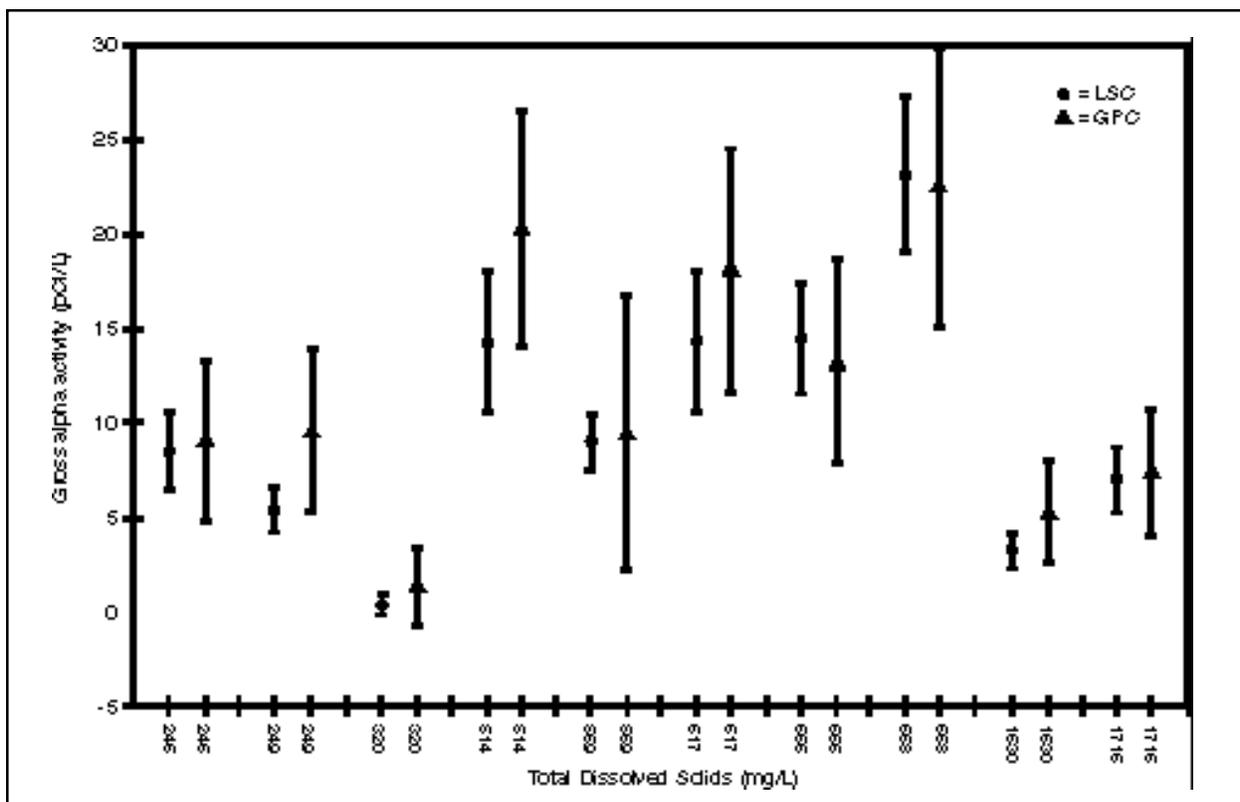
**Table 8.**

<sup>226</sup>R uptake from 100 mL simulated ground water matrix.

Sample ID.	NWQL Results by GPC (pCi/L)		Eckrom Results by LSC (pCi/L)	
		2 sigma TPO		2 sigma TPO
Sample 1	7.37	3.46	6.84	2.11
Sample 2	5.13	2.72	2.99	1.07
Sample 3	9.16	4.27	8.53	2.53
Sample 4	9.61	4.39	5.38	1.74
Sample 5	9.36	7.36	8.84	2.59
Sample 6	0.770	0.901	0.780	0.320
Sample 7	3.20	2.71	2.51	0.91
Sample 8	1.26	2.07	0.57	0.22
Sample 9	22.5	7.4	23	5.68
Sample 10	13.1	5.4	14.22	3.82
Sample 11	0.306	0.135	-0.310	0.140
Sample 12	2.25	1.16	2.13	0.80
Sample 13	9.96	5.15	5.22	1.68
Sample 14	1.10	2.27	0.930	0.390
Sample 15	2.69	1.38	2.06	0.78
Sample 16	-0.808	1.44	1.97	0.75
Sample 17	3.36	2.71	-0.470	0.240
Sample 18	5.47	5.42	0.470	0.190
Sample 19	17.9	6.5	14.2	3.8
Sample 20	-0.268	0.831	0.240	0.100
Sample 21	20.2	6.2	14.2	3.8
Sample 22	2.22	2.36	0.400	0.170
Sample 23	1.01	2.08	0.470	0.190
Sample 24	1.24	0.78	1.73	0.20

**Table 9.**

Comparative results for NWQL water samples using GPC and LSC.



**Figure 4.**

Comparison of paired results at varying TDS levels: LSC (left) and GPC (right).

The results for the ten which had been characterized for TDS content are shown in Figure 4. In this figure, the gross alpha activity for each sample measured by the two methods is plotted on the y-axis versus the TDS content on the x-axis. Results by the two methods are plotted in pairs: the left-hand data point in each pair is the LSC result; the right-hand data point in each pair is the GPC result. The error bars reflect 2 sigma total propagated uncertainty (95% confidence interval). Note that in every case, the agreement between the 95% confidence intervals is excellent and appears to be unaffected by the amount of dissolved solids in the samples. Also the TPU of the LSC results is lower in all cases.

## Conclusion

In conclusion, the proposed method for measuring gross alpha activity by extraction chromatography and liquid scintillation counting is quick and allows for lower detection limits with shorter count times. The measurement of actinides elements is excellent using 500 mL sample aliquots. Accurate measurement of alpha activity due to radium requires a sample aliquot of 100 mL if calcium content is high. A detection limit of 2 pCi/L (75 mBq/L) can be achieved with a 60 minute count time and a 100 mL sample. Process samples (non-environmental) in which the alpha activity is due only to the actinides and not to radium can be analyzed by this procedure using 500 mL aliquots. Detection limits for these sample sizes would be much lower, in the range of 15 mBq/L.

## References

1. Horwitz, E.P. et al. (1993). Separation and preconcentration of actinides from acidic media by extraction chromatography. *Analytica Chimica Acta*. 281:361-372.
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3. Horwitz, E.P. et al. (1997). Dipex: A new extraction chromatographic material for the separation and preconcentration of actinides from aqueous solution. *Reactive & Functional Polymers*.