

# Complex sample preparation using the tritium column

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# Aim

The analysis of aqueous samples containing high tritium content whilst enabling subsequent analysis of a range of alpha, beta and gamma fission/activation products.

## Tritium

Cs-137 Cs-134 Co-60  
Sb-125 Ru-106 Sr90  
I-129 Tc-99 Ni-63  
Am-241 Pu isotopes Np-237  
U isotopes Th isotopes  
gross alpha beta

# Objectives

- Avoid tritium contamination during radiochemical analysis
- Achieve detection limits across 6 orders of magnitude for more than 7 radioanalytical techniques
- Simplified chemistry to avoid incompatibilities

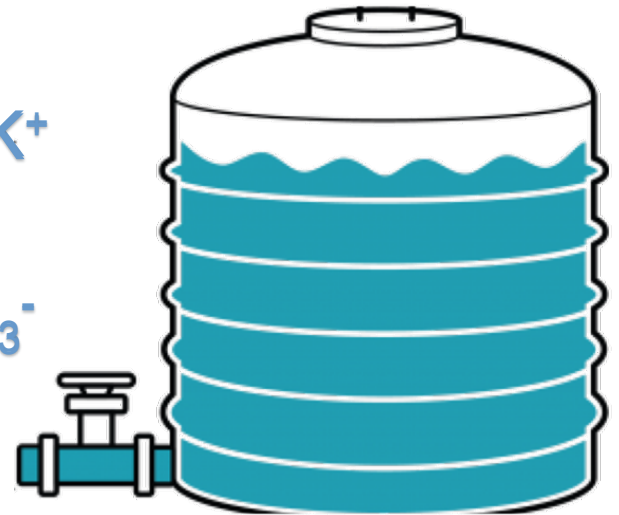
# Sample chemistry

## Process water sample

- Resulting from chemical treatment
- High cation/anion content
- pH 7-8

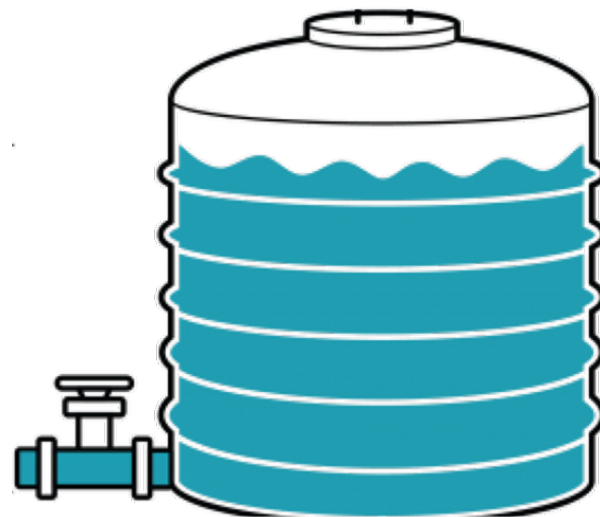
$\text{Ca}^+$   $\text{Mg}^+$   $\text{Na}^+$   $\text{K}^+$

$\text{HCO}_3^-$   $\text{Cl}^-$   $\text{SO}_3^-$



# Sample radionuclide content

<b>Tritium H-3</b>	<b><math>1 \times 10^5</math> Bq/L</b>
Gamma emitters (Cs-137, Cs-134, Co-60, Sb-125, Ru-106)	~0.5 Bq/L
Sr-90	~2 Bq/L
I-129	~2 Bq/L
C-14	~10 Bq/L
Ni-63	~2 Bq/L
Tc-99	~1 Bq/L
Gross $\beta$	~10 Bq/L
Gross $\alpha$	~0.05 Bq/L



# Measurement Quality Objectives

Radioisotope	MDL Bq/L	Uncertainty %
Tritium H-3	100	<20
Gamma emitters (Cs-137, Cs-134, Co-60, Sb-125, Ru-106)	0.0005	<5
Sr-90	0.02	<5
I-129	0.03	<5
C-14	0.05	<5
Ni-63	0.05	<5
Tc-99	0.02	<5
Gross $\beta$	0.1	<25
Gross $\alpha$	0.06	<25



# Analysis procedures

- Liquid scintillation counting
- Gas-flow proportional counter
- Gamma spectrometry
- Alpha spectrometry

Different source preparations  
Different interferences

Fit-for-purpose procedure with simple chemistry

# Tritium analysis

## Proficiency Test sample – Eichrom method

### Reported Activity Concentrations

Tritium	$29.8 \pm 3.5$ Bq/L
Sr-90	$12.3 \pm 2.1$ Bq/L
Cs-137	$32.6 \pm 4.1$ Bq/L
Am-241	$8.3 \pm 1.4$ Bq/L





# Tritium analysis

## Proficiency test sample – H-3 results

Sample ID	Bq/L	Uncert. k=2	% uncert.	Recovery %
S1	26.0	5.3	20.4	87.3
S2	25.5	5.2	20.6	85.4
S3	32.7	6.2	18.8	110.0
S4	29.3	5.6	19.2	98.3
S5	31.5	5.9	18.6	105.7
<b>AVERAGE</b>				
	<b>29.0</b>	<b>5.6</b>	<b>19.5</b>	<b>97.3</b>
Std Dev	3.2			10.8
Std Dev %	11.1			11.1

# Mixed Gamma Experiments

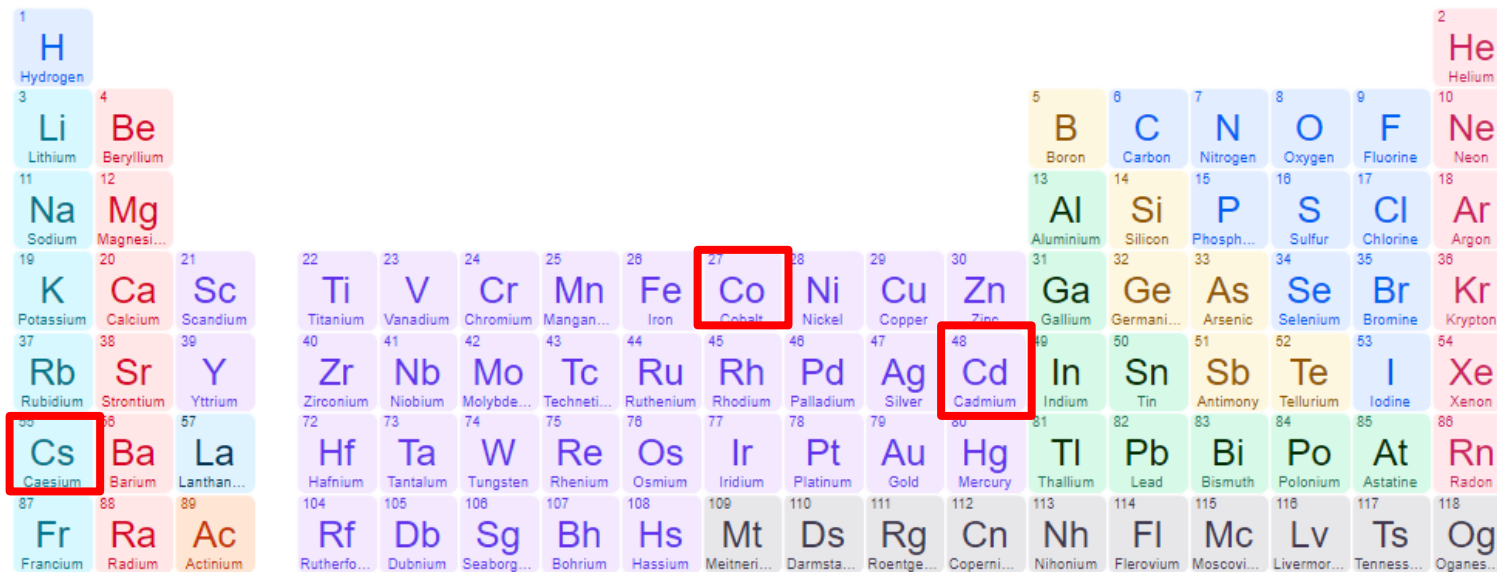
Gamma screening is quick and easy!

Not susceptible to chemical changes like LSC or GFPC!

## Mixed gamma sample

<b>Nuclide</b>	<b>Bq/g</b>	<b>Bq/test (25 ml)</b>
Am-241	0.40	10.08
Cd-109	0.22	5.50
Cs-137	0.19	4.68
Co-60	0.15	3.69

# Mixed Gamma Experiments



A periodic table of elements with four specific elements highlighted by red boxes: Cobalt (Co), Cadmium (Cd), Caesium (Cs), and Americium (Am). The table is color-coded by groups and periods.

1																	2				
H																	He				
Hydrogen																	Helium				
3	4															5	6	7	8	9	10
Li	Be															B	C	N	O	F	Ne
Lithium	Beryllium															Boron	Carbon	Nitrogen	Oxygen	Fluorine	Neon
11	12															13	14	15	16	17	18
Na	Mg															Al	Si	P	S	Cl	Ar
Sodium	Magnesium															Aluminium	Silicon	Phosphorus	Sulfur	Chlorine	Argon
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36				
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr				
Potassium	Calcium	Scandium	Titanium	Vanadium	Chromium	Manganese	Iron	Cobalt	Nickel	Copper	Zinc	Gallium	Germanium	Arsenic	Selenium	Bromine	Krypton				
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54				
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe				
Rubidium	Strontium	Yttrium	Zirconium	Niobium	Molybdenum	Technetium	Ruthenium	Rhodium	Palladium	Silver	Cadmium	Indium	Tin	Antimony	Tellurium	Iodine	Xenon				
55	56	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86				
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn				
Caesium	Barium	Lanthanum	Hafnium	Tantalum	Tungsten	Rhenium	Osmium	Iridium	Platinum	Gold	Mercury	Thallium	Lead	Bismuth	Polonium	Astatine	Radon				
87	88	89	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118				
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og				
Francium	Radium	Actinium	Rutherfordium	Dubnium	Seaborgium	Bohrium	Hassium	Meitnerium	Darmstadtium	Roentgenium	Copernicium	Nihonium	Flerovium	Moscovium	Livermorium	Tennessee	Oganesson				

58	59	60	61	62	63	64	65	66	67	68	69	70	71
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Cerium	Praseodymium	Neodymium	Promethium	Samarium	Europium	Gadolinium	Terbium	Dysprosium	Holmium	Erbium	Thulium	Ytterbium	Lutetium
90	91	92	93	94	95	96	97	98	99	100	101	102	103
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
Thorium	Protactinium	Uranium	Neptunium	Plutonium	Americium	Curium	Berkelium	Californium	Einsteinium	Fermium	Mendelevium	Nobelium	Lawrencium

# Removal of 'interferences'

## Tritium column resins

- Diphonix® (Monophos) targeting cations
- AG 1x8, Cl<sup>-</sup> form targeting anions
- Polymethacrylate resin targeting organic molecules

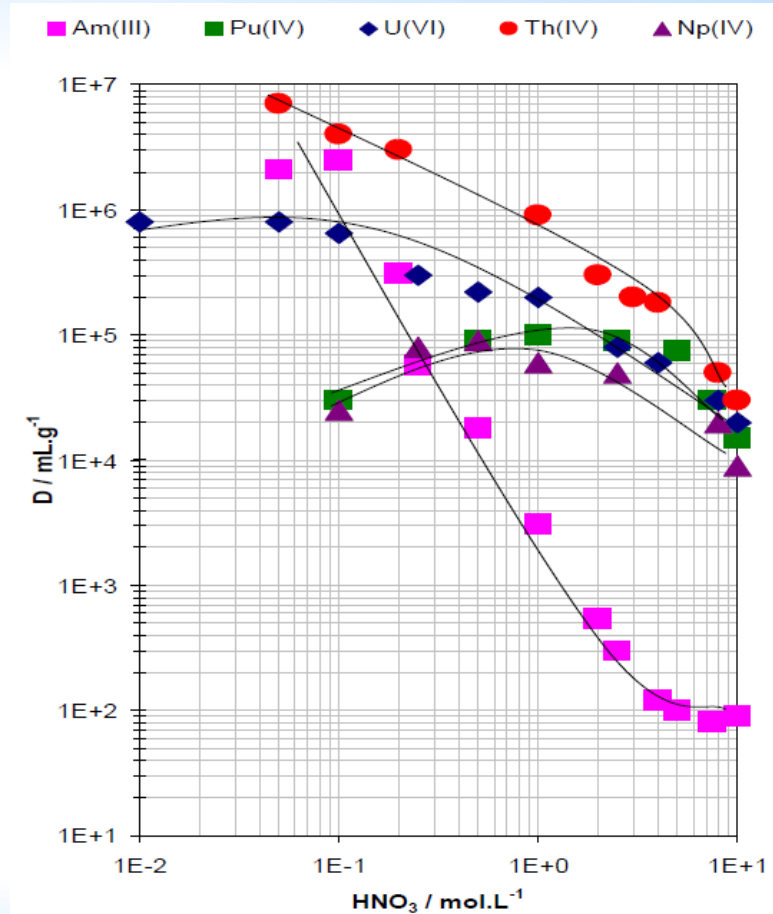
Radioisotope cations adsorbed to Diphonix (Monophos)

Elution from chelating ion exchange resin requires redox reaction or excess reactive reagent.

# Potential elutions

## Diphonix resin $K_d$

- Nitric acid
- Phosphoric acid
- Chelating ligand?



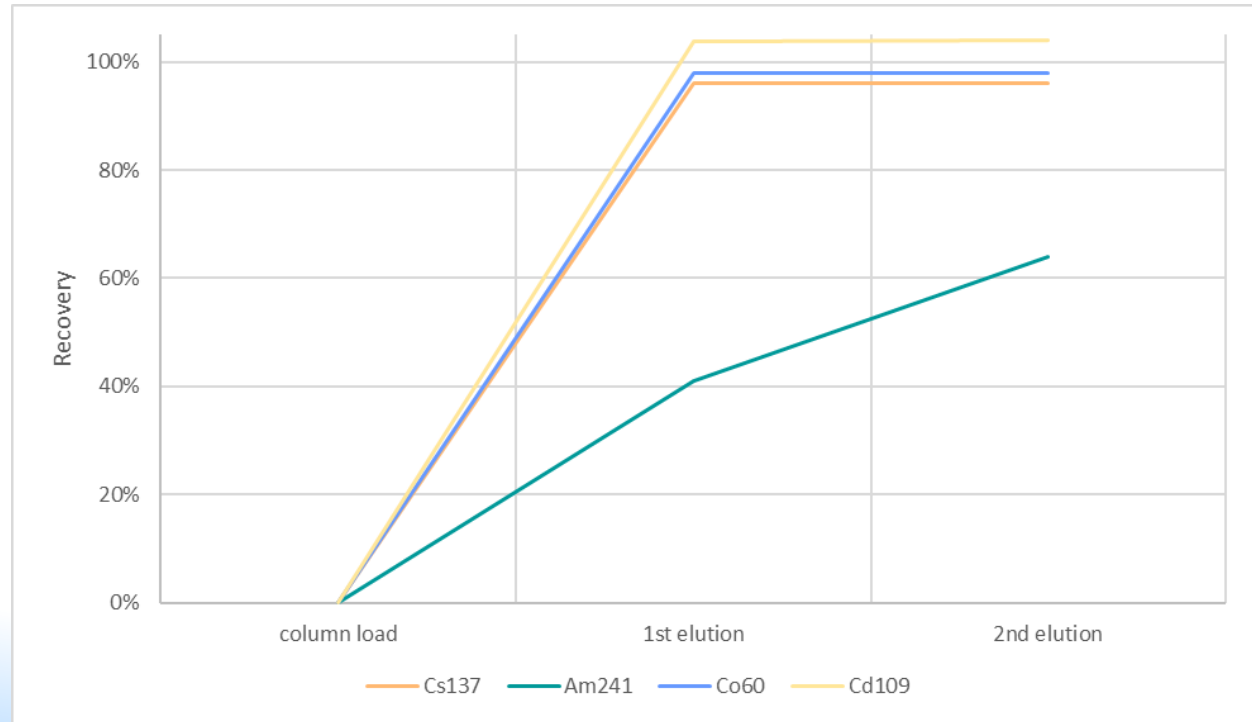
# HNO<sub>3</sub> elution

1. 25 mL load solution
2. 15 mL 9M HNO<sub>3</sub>

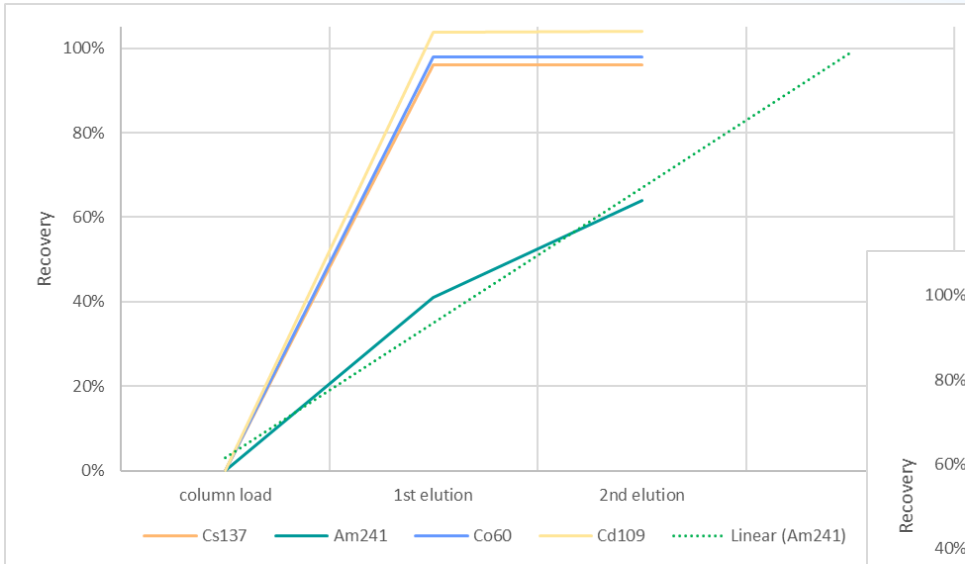
Radioisotope	Column Load CPS	1st elution CPS	Recovery
Cs-137	0.000	0.1678	97%
<b>Am-241</b>	<b>0.000</b>	<b>0.2250</b>	<b>41%</b>
Co-60	0.000	0.0880	97%
Cd-109	0.000	0.0828	104%

# 2<sup>nd</sup> HNO<sub>3</sub> elution

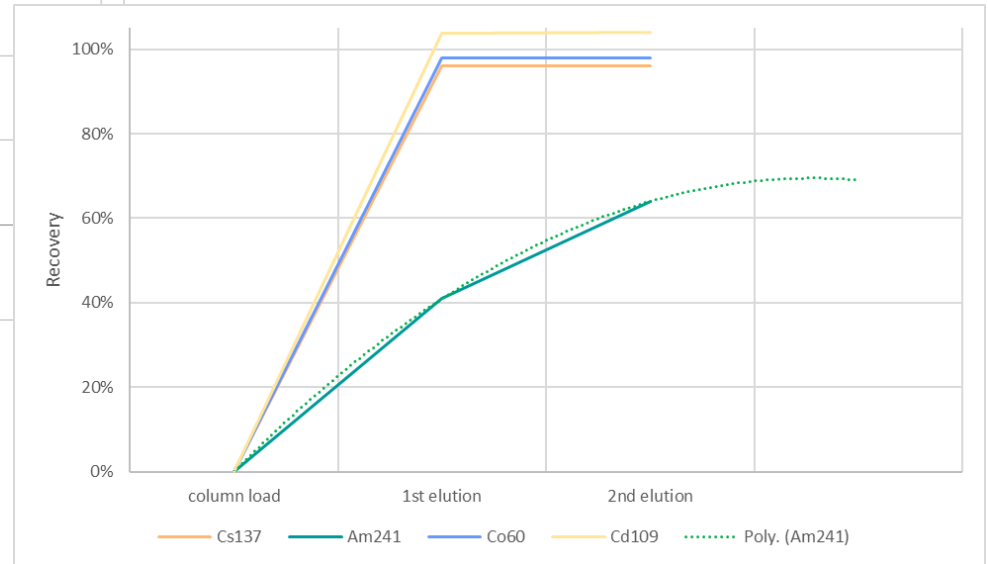
1. 25 mL load solution
2. 15 mL 9M
3. 15 mL 9M



# More HNO<sub>3</sub> elutions?



Could it be this simple?





# Preliminary conclusions

## Main points:

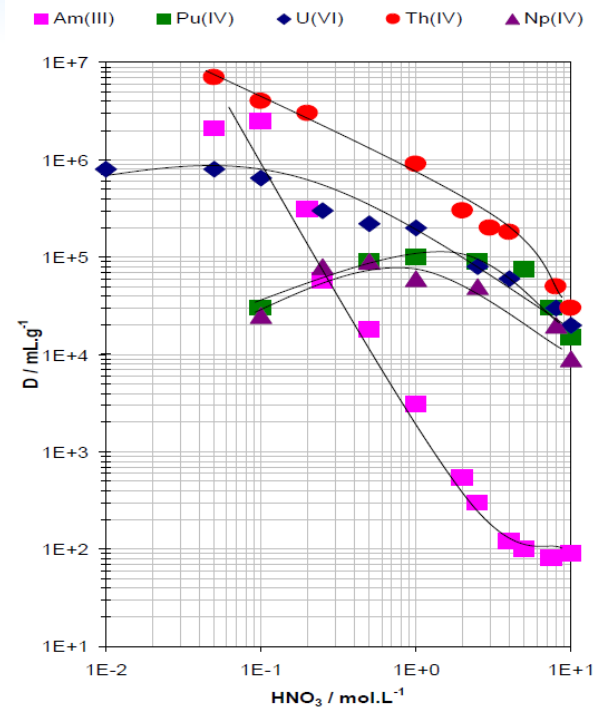
- Cs-137 recovery was acceptable at 97%
- Co-60 recovery was acceptable at 97%
- Cd-109 recovery was acceptable at 104%
- Am-241 was 41-54% with an initial elution of 15ml 9M HNO<sub>3</sub>
- An additional 15ml of 9M HNO<sub>3</sub> resulted in an overall recovery of 56-64%

The combination of Diphonix/Monophos and AG 1x8 resins is an effective sample pre-treatment for the separation of tritium from remaining fission/activation products.

Further work is required to determine the acceptable and repeatable recovery for actinides (Am-241).

# Further work

- Testing with actinides of more complicated chemistry
- Investigation of oxidizing acids e.g.  $\text{H}_3\text{PO}_4$
- Investigation of 'light' complexing agents e.g. oxalic acid



# Further work

- Development of a QC sample for monitoring the efficiency of elutions
- Testing compatibility with subsequent radiochemical analyses e.g. Sr-90, Ni-63, I-129, Tc-99
- Repeatability and robustness testing for complete validation

*Thank you!*

