The use of $^{99}$Mo/$^{99m}$Tc generators in the analysis of low levels of $^{99}$Tc in environmental samples by radiochemical methods

Based on the following papers...

Why the interest in $^{99}\text{Tc}$?

- Fission product of uranium - beta decay of $^{99}\text{Mo}$
- Half life - 213,000 y
- Specific activity of 630 kBq/mg
- Beta decay - stable $^{99}\text{Ru}$
- Can exist naturally - spontaneous fission of $^{238}\text{U}$
- Fallout from nuclear weapon testing
- Main source - nuclear industry
- Discharges from nuclear reprocessing...

Decay scheme of $^{99}\text{Mo}$
Discharges of $^{99}$Tc from nuclear reprocessing

**Sellafield**
- Since 1950’s
- Peak discharges
  - 1970’s – 180 TBq/a
  - 1990’s – 192 TBq/a (EARP)
- Total discharged - **1.7 PBq**

**Cap la Hague**
- Since 1960’s
- Peak discharges
  - mid 1980’s – 25.9 TBq/a
- Total discharged - **128 TBq**

Recent annual discharges
- Sellafield 2.4 TBq - 2008
- Cap la Hague < 0.5 - 2006
Enhanced Actinide Removal Plant (EARP)

- Designed to treat high level nuclear wastes from Magnox reprocessing plants
- Designed to remove Pu, Cs and Sr isotopes

However...
- $^{99}$Tc in waste present as pertechnate ($\text{TcO}_4^{-}$)
- Difficult to remove

Resulting in...
- 50 fold increase in $^{99}$Tc discharges from 1990 to 1996...
- As treatment of stored waste from previous years was processed...
Long range oceanic transport of $^{99}$Tc

TcO$_4^-$
- Soluble
- Highly conservative in seawater (under oxic conditions)

Transport times from Sellafield
- North Sea 1-3 years
- N. Norway 3-5 years
- Barents Sea 4-6 years
- Svalbard 5-7 years
Long range oceanic transport of $^{99}$Tc

Hillesøy

- Discharge Sellafield
- Tc-99 in F. vesiculosus
Simulation of transport of $^{99}$Tc discharges

Surface water concentrations (NAOSIM)

- 1993 – Pre EARP
Real observations in seawater

Higher concentrations of $^{99}$Tc observed along southern coast of Norway than in the North...

Maximum levels observed
- Hillesøy - 1.93 Bq/m$^3$
- Bjørnøya - 0.35 Bq/m$^3$
- Hopen - 0.32 Bq/m$^3$
- Ny Ålesund - 0.25 Bq/m$^3$
- Jan Mayen - 0.14 Bq/m$^3$
Accumulation by marine biota

$^{99}$Tc accumulates to varying degrees in marine biota

- Seaweeds (brown)  \( CF \ 1 \times 10^5 \)
- Lobsters  \( CF \ 1 \times 10^2 \) to \( 1 \times 10^5 \)
  (organ/sex differences)
- Molluscs  \( CF \ 1 \times 10^2 \)
- Fish  \( CF \ 1 \times 10^1 \)

- Tracer studies - uptake from food and water and transfer through foodchain
- Uptake of $^{99}$Tc by man \( (f_1 \ 0.1-0.5) \)
- Committed effective dose per unit intake (Sv/Bq)
  \( ^{99}$Tc - \( 6.4 \times 10^{-10} \) \( ^{137}$Cs - \( 1.3 \times 10^{-8} \)
- Seaweed in health food shops - (C.F.I.L. -1250 Bq/kg)
Analysis of $^{99}$Tc by NRPA

Using the method of Chen et al. (2001)

$^{99m}$Tc as a yield tracer

3-4 days to complete

**Day 1**

Seawater sample filtered

50 or 100 l samples

**Day 2**

Tracer added and samples pumped at 40ml/min through column

Biorad AG1-X4 resin

50 l per column

Pumping 21 hours...
Analysis of $^{99}$Tc by NRPA

Day 3
Column washed (removes Ru isotopes)
- 100 ml H$_2$O
- 50 ml 1M NaOH-0.1 M EDTA+10 ml 15% NaClO
- 150 ml 1 M NaOH-0.1 M EDTA+10ml 15% NaClO
- 100ml 1 M NaOH
- 100 ml H$_2$O
- 500 ml 1 M HNO$_3$

Tc-99 fraction stripped from column
- 200 ml conc. HNO$_3$ + 1 ml 3 M NaNO$_3$
Analysis of $^{99}$Tc by NRPA

Day 3 (continued)
Eluted fraction treated further to scavenge U, Th, Pu, Am and Po

- Evaporation to < 1 ml avoiding dryness
- Add 0.5 ml 5 M H$_2$SO$_4$
- Add 19 ml H$_2$O
- Add 2 ml 15% NaClO. Heat for 10 minutes
- Add 40 ml H$_2$O
- Add 2 drops 10 mg/ml AgNO$_3$
- Add 0.5 ml 10 mg/ml FeCl$_3$
- pH adjustment: pH 9 with 6M NaOH
- Filter (Whatman GF/A) into 250 ml separating funnel to remove precipitate
Analysis of $^{99}$Tc by NRPA

Day 3 (continued)
Filtrate further purified...

- Add 10 ml 10M $\text{H}_2\text{SO}_4$
- Add 2 g $\text{K}_2\text{S}_2\text{O}_8$
- Bring to approx. 100 ml with $\text{H}_2\text{O}$
- Add 80 ml 5% Tri-isooctylamine in xylene - Shake 10 mins
- Discard aqueous phase
- Add 80 mls $\text{H}_2\text{O}$ - Shake 5 mins.
- Discard aqueous phase
- Add 80 mls $\text{H}_2\text{O}$. Shake 5 mins.
- Discard aqueous phase
- Add 20 mls 2 M $\text{NaOH}$. Shake 2 mins.
- Collect aqueous phase
- Add 5 mls 0.5 M $\text{NaOH}$. Shake 2 mins.
- Collect and bulk aqueous phase
- Evaporate to 20 mls

$^{99}$Tc to organic phase

$^{99}$Tc to aqueous phase
Analysis of $^{99}\text{Tc}$ by NRPA

Day 3 (continued)
Electrodeposition on to steel planchettes
- 300 mA - 12 hours

Day 4
- Determine yield - gamma ($^{99m}\text{Tc}$)
- Planchettes packed for beta counting

Beta Counting
- Planchettes counted after atleast 1 week…
- Count times - 40 hours
- Low background anti-coincidence gas flow beta counter
Something strange was going on…

Main office
- Seawater samples from North Sea
- High levels of $^{99}$Tc!

Tromsø
- Seawater samples from Norwegian Arctic
- Low levels of $^{99}$Tc!
- Set up the same method as used in Oslo
- Early results were often higher than expected
- The only likely culprit was the source of the $^{99m}$Tc tracer…
**99Mo/99mTc generators**

- 99mTc obtained from 99Mo/99mTc generators
- Produced for hospitals - 99mTc nuclear imaging
- Readily available - relatively cheap to use
- 99Mo loaded onto alumina column - irradiated Mo
- 99mTc (as TcO4⁻) eluated out using a 0.9% NaCl solution
- Produced with a range of initial activities

**Tromsø**

- 20 to 30 GBq to hospital
- ~100 MBq when taken to laboratory
- 20-30 kBq 99mTc per sample
- <0.1 mBq of 99Tc from decay of 99mTc
- Negligible impact on analytical result!
Assumption held…

It was assumed that the tracer solution eluated from $^{99}$Mo/$^{99m}$Tc generators:

- Did not contain any additional $^{99}$Tc
- Did not contain any other source of $^{99}$Tc (other than $^{99m}$Tc) i.e. $^{99}$Mo
- Did not contain any other beta emitters…

Yield determination in method of Chen et al. (2001) relies on comparison between:

- Change in activity of a stored tracer solution
  - by physical decay
- Change in activity on the tracer added to the sample
  - by physical decay + analytical loss

…as determined by gamma emission of $^{99m}$Tc (140 keV)
Assumptions can be wrong…

A check of the literature revealed a number of studies highlighting problems with the use of $^{99}$Mo/$^{99m}$Tc generators and possible impurities in the eluate.

Possible contaminating radionuclides:

$^{89}$Sr, $^{90}$Sr, $^{95}$Nb, $^{95}$Zr, $^{103}$Ru, $^{106}$Ru, $^{125}$Sb, $^{131}$I, $^{132}$I, $^{137}$Cs, $^{140}$Ba, $^{140}$La, $^{181}$W, $^{185}$W…

Separation process and low activity means that these should have no impact…

But… $^{99}$Mo and $^{99}$Tc can also be eluated!

Can effect both the activity of $^{99}$Tc plated and the yield determination!

From 1970
Breakthrough of $^{99}$Tc…

Tracer only solutions processed as per normal samples:

- 1-10 mBq/g of $^{99}$Tc from tracer
- 0.2-1.0 g of tracer per sample
- 50 l seawater sample
- 0.1-0.2 Bq/m$^3$ $^{99}$Tc
- 5-10 mBq of $^{99}$Tc

- Tracer contribution can have a significant impact!
How to solve the problem...

Can we calculate the possible concentration of $^{99}$Tc in a tracer solution at any given time?

Holland et al. (1986)

- Compared actual ratios of (moles total Tc/mCi $^{99m}$Tc) versus theoretical calculations (based on initial activity and eluation history)
- Theoretical values underestimated the mass of total Tc by 25-300%
- Partly due to assumption in theoretical calculations that 100% of $^{99m}$Tc is eluated
- Not the case in reality + but also due to eluation of $^{99}$Tc
- Variation between generators from different manufacturers...
- Theoretical approach not valid...
How to solve the problem...

Plating of tracer solution and beta counting not an option due to contaminating beta emitters… e.g. Ru-103 (half life 40 days)

- 2 week old 25 GBq generator
- Eluates collected over a 3 week period from normal operations
- Decayed for 10 days after last eluate added
- Analysed by high resolution gamma

497.1 keV Ru-103  511 keV annihilation line

- No $^{99}$Mo lines seen in this test…
Breakthrough of $^{99}$Mo...

$^{99}$Mo detected in 29 eluates from a new 4 GBq generator (4 GBq) over 17 days by gamma (high activities only) and LSC

- 1st 8 eluates in 1st 24 hours
- 330-1000 Bq per eluate
- Eluates after 2 weeks (Nos. 22-29)
- 4-7 Bq per eluate
- High activity effect?
- Effect variable depending on 'history' of generator?
How to solve the problem...

Run blanks...
- Process 50 l of distilled water with each sample run
- Subtract contribution of $^{99}$Tc from tracer as measured in blank
- Produce corrected $^{99}$Tc values...

However...
- Really LOW level samples...
- Swamping of sample $^{99}$Tc signal with tracer $^{99}$Tc...
- Problem of $^{99}$Mo breakthrough...

<table>
<thead>
<tr>
<th>$^{99}$Tc activity (Bq/m$^3$)</th>
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</tr>
</thead>
<tbody>
<tr>
<td>No correction</td>
<td>With correction</td>
</tr>
<tr>
<td>0.26 ± 0.03</td>
<td>0.25 ± 0.03</td>
</tr>
<tr>
<td>0.26 ± 0.03</td>
<td>0.23 ± 0.03</td>
</tr>
<tr>
<td>0.10 ± 0.01</td>
<td>0.08 ± 0.01</td>
</tr>
<tr>
<td>0.30 ± 0.03</td>
<td>0.24 ± 0.04</td>
</tr>
<tr>
<td>0.05 ± 0.01</td>
<td>&lt; 0.05</td>
</tr>
<tr>
<td>0.28 ± 0.03</td>
<td>0.20 ± 0.04</td>
</tr>
<tr>
<td>0.12 ± 0.01</td>
<td>0.08 ± 0.02</td>
</tr>
<tr>
<td>0.31 ± 0.03</td>
<td>0.27 ± 0.04</td>
</tr>
<tr>
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<td>0.08 ± 0.01</td>
</tr>
<tr>
<td>0.30 ± 0.03</td>
<td>0.26 ± 0.04</td>
</tr>
<tr>
<td>0.29 ± 0.03</td>
<td>0.25 ± 0.04</td>
</tr>
<tr>
<td>0.18 ± 0.02</td>
<td>0.14 ± 0.03</td>
</tr>
</tbody>
</table>
How to solve the problem...

For really low level samples it maybe necessary to remove any contaminating $^{99}$Tc and $^{99}$Mo...

Hou et al. (2007)

- Either by TEVA chromatography
- Or with Alumina cartridge filtration (x2)
- Both methods remove $^{99}$Tc and $^{99}$Mo
- Alumina cartridge easier and quicker to use - important due to high dose rates from $^{99m}$Tc...
- No need to correct for contribution of $^{99}$Tc from tracer
- Practical advice: always wash generator before taking eluate...

<table>
<thead>
<tr>
<th>Volume (l)</th>
<th>$^{99}$Tc (Bq/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>175</td>
<td>0.0571</td>
</tr>
<tr>
<td>176</td>
<td>0.0502</td>
</tr>
<tr>
<td>200</td>
<td>0.0458</td>
</tr>
<tr>
<td>200</td>
<td>0.0572</td>
</tr>
<tr>
<td>200</td>
<td>0.0264</td>
</tr>
<tr>
<td>186</td>
<td>0.0263</td>
</tr>
<tr>
<td>200</td>
<td>0.0476</td>
</tr>
</tbody>
</table>

Seawater from Greenland
5-10 mBq per sample
NRPA $^{99}$Tc intercomparison - 2005

Low level seawater sample…

![Graph showing the comparison of $^{99}$Tc levels across different labs. The x-axis represents the lab code number, and the y-axis represents $^{99}$Tc concentration in Bq/m$^3$. There are error bars indicating the range of measurement uncertainty at +1 sigma and -1 sigma. The median value is circled.]
In conclusion…

With the use $^{99}\text{Mo}/^{99m}\text{Tc}$ generators - need to be aware of contamination problems with $^{99}\text{Tc}$ and $^{99}\text{Mo}$ in the eluate…

Take appropriate actions to mitigate the problem…

Can depend on expected concentration in sample…

In general…
Always question assumptions!

Always check the literature - problems may have already been reported and discussed…
Further reading…
