Statens strålevern
Norwegian Radiation Protection Authority

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

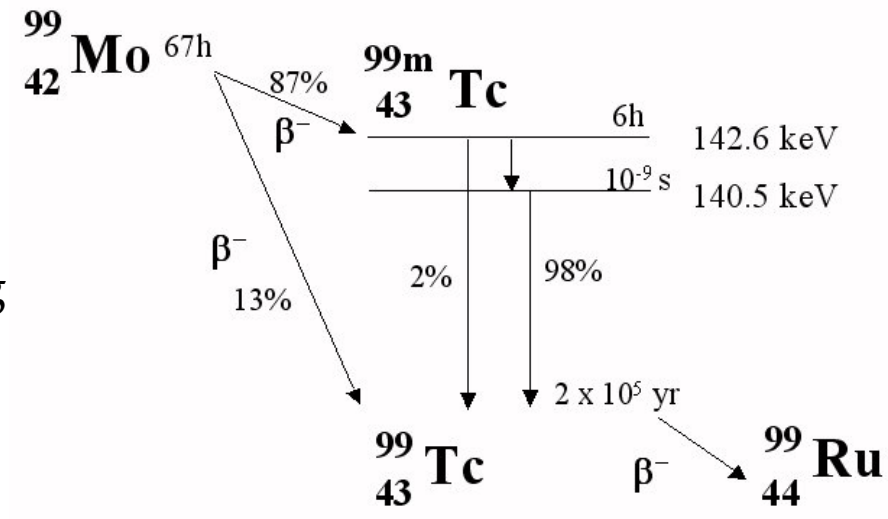
Based on the following papers…

Dowdall M., Gwynn J.P., Selnæs Ø.G. and Lind B. (2004) Water, Air and Soil Pollution

Hou X., Jensen, M. and Nielsen S.P. (2007) Applied Radiation and Isotopes

Why the interest in ^{99}Tc?

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



Decay scheme of ^{99}Mo

Discharges of ^{99}Tc from nuclear reprocessing

Sellafield

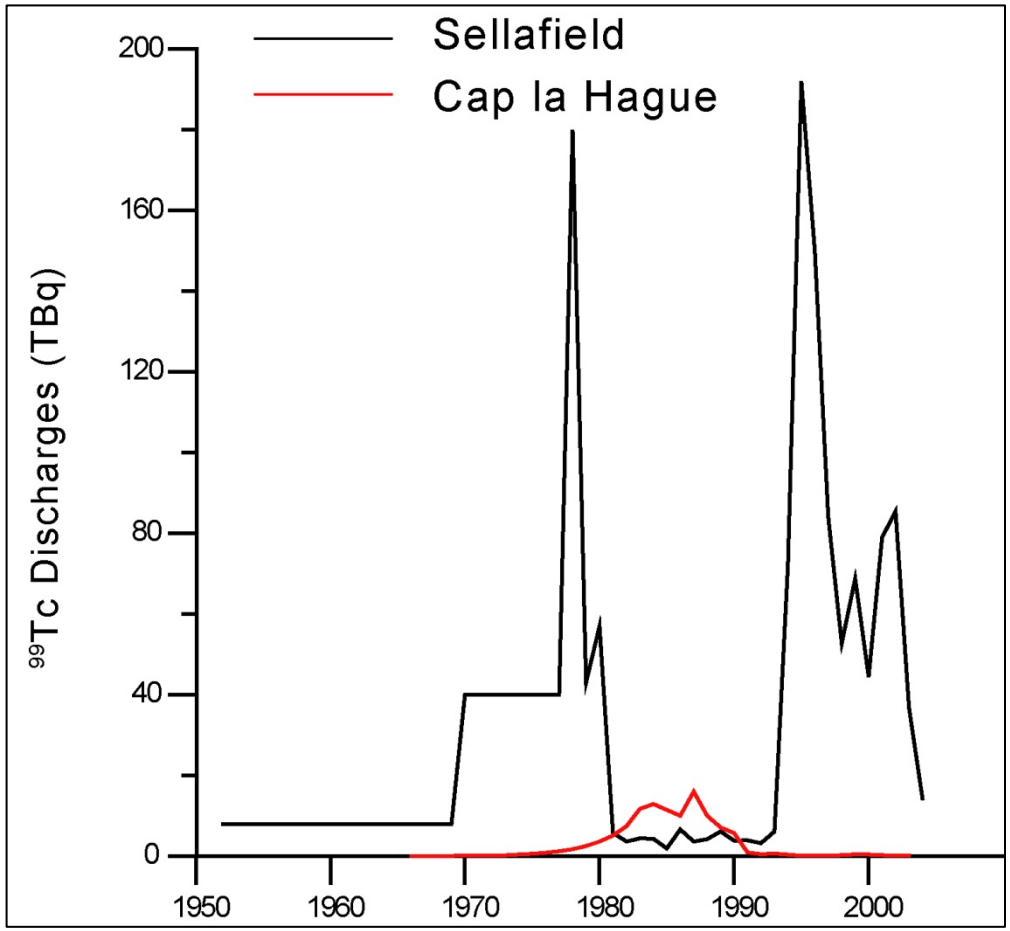
- Since 1950's
- Peak discharges
  - 1970's – 180 TBq/a
  - 1990's – 192 TBq/a (EARP)
- Total discharged - **1.7 PBq**

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 (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

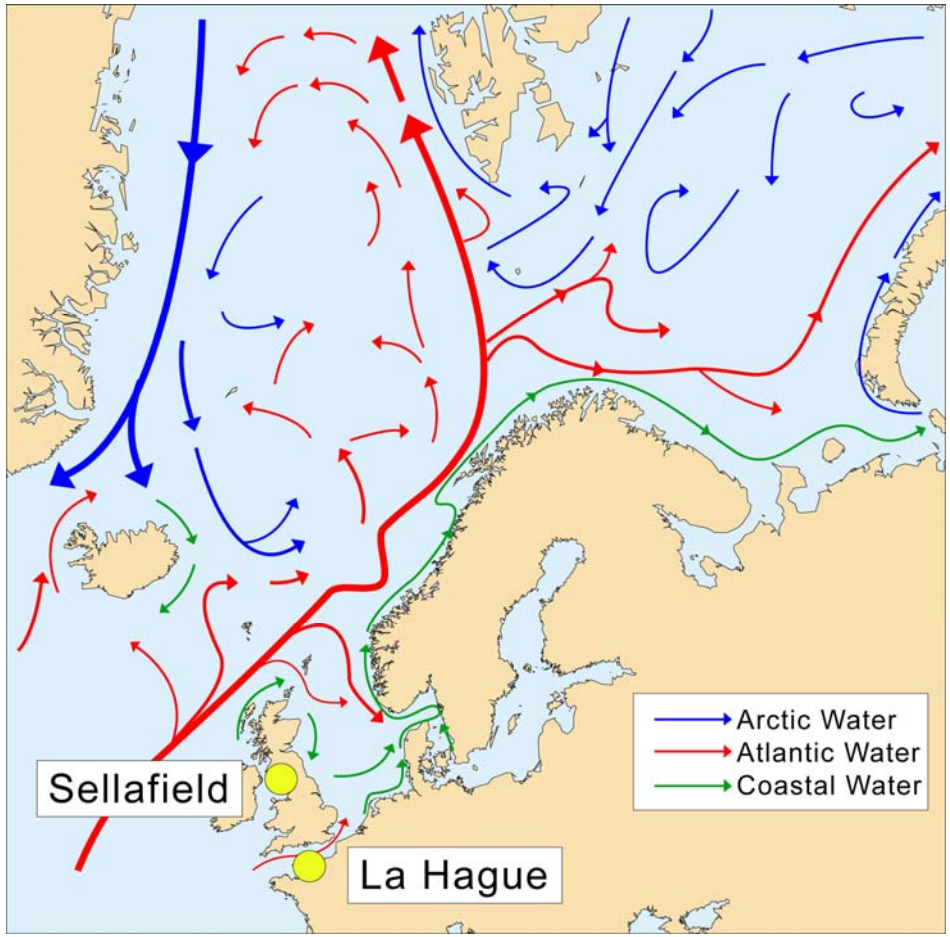
<u>TcO^{4-}</u>

- Soluble
- Highly conservative in seawater

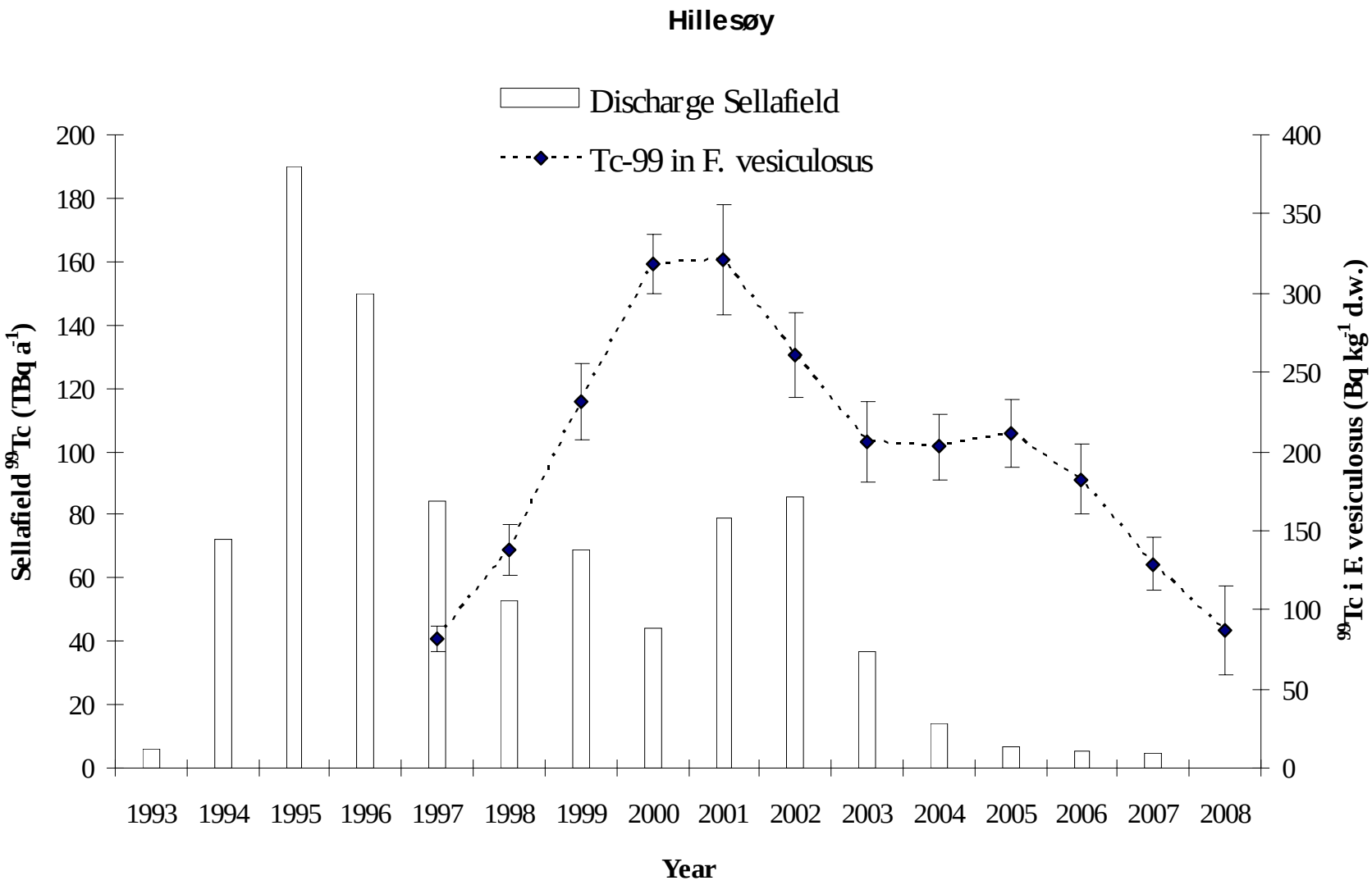
(under oxic conditions)

Transport times from Sellafield

- North Sea 1-3 years
- N. Norway 3-5 years
- Barents Sea 4-6 years
- Svalbard 5-7 years



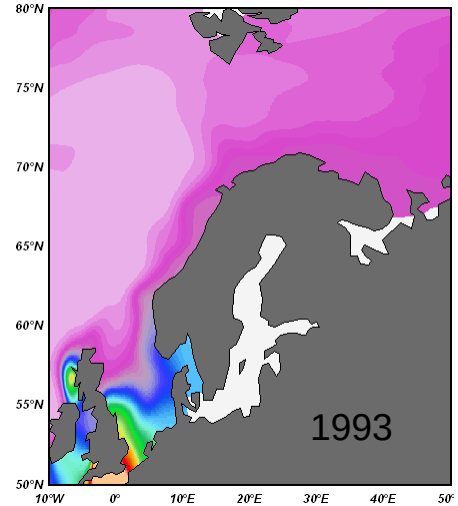
Long range oceanic transport of ^{99}Tc

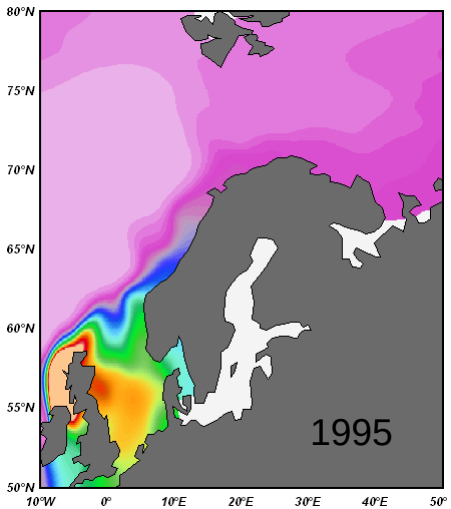


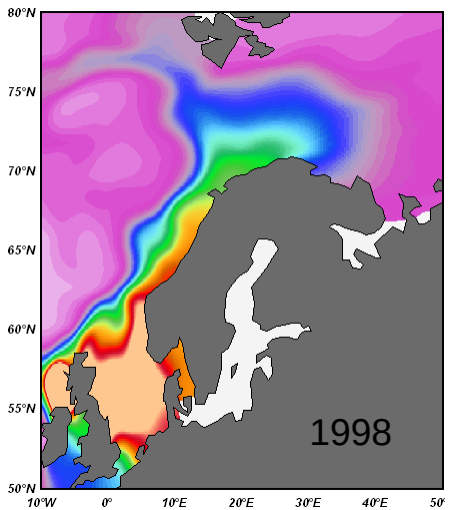
Simulation of transport of ^{99}Tc discharges

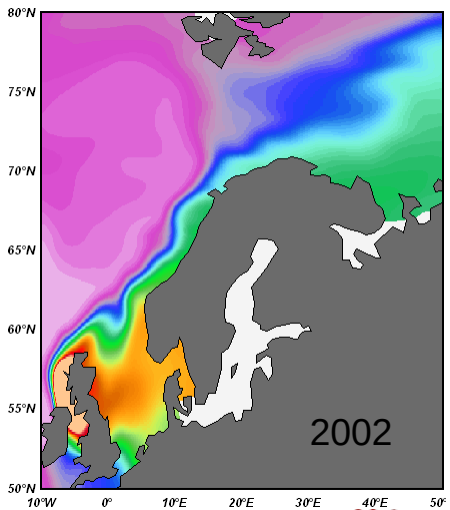
Surface water concentrations (NAOSIM)

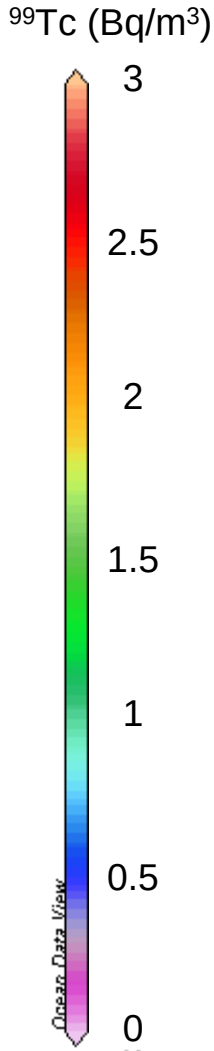
- 1993 – Pre EARP
- 1995, 1998 & 2002 – Post EARP











Real observations in seawater

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

<u>Maximum levels observed</u>

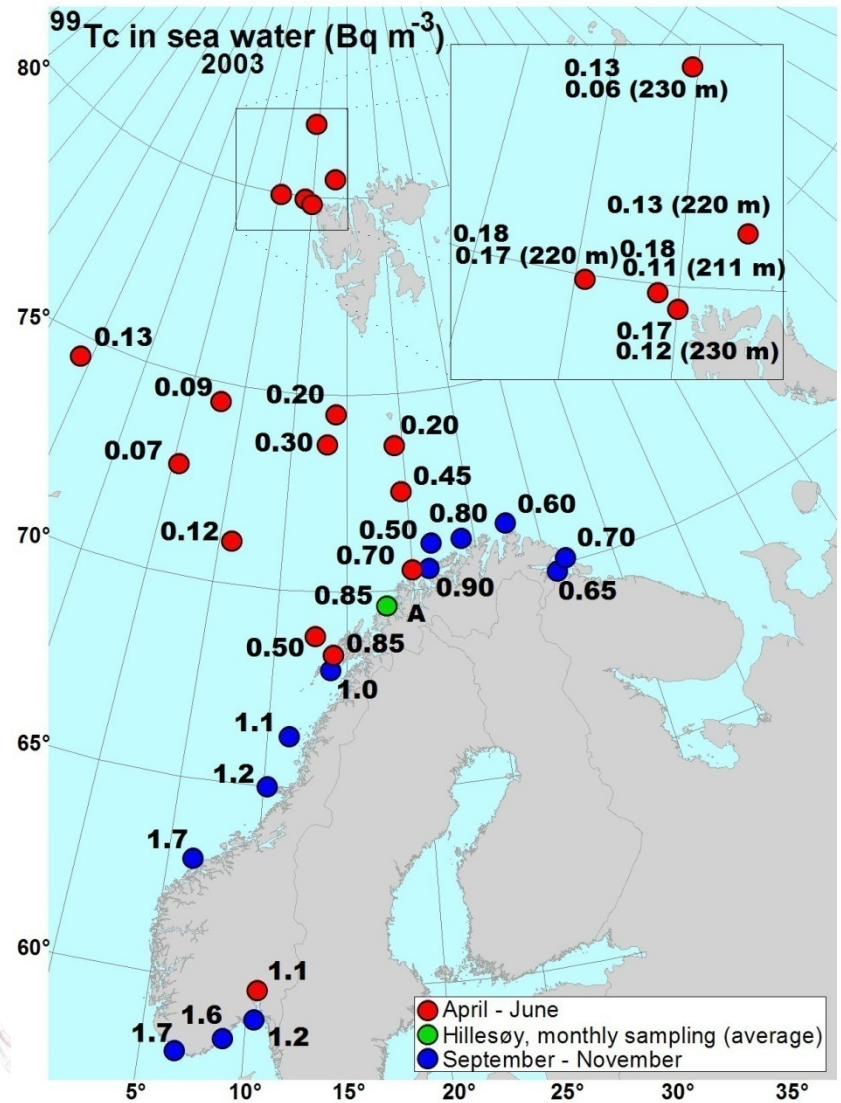
Hillesøy - 1.93 Bq/m^3

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 x 10^5
- Lobsters CF 1 x 10^2 to 1 x 10^5
  (organ/sex differences)
- Molluscs CF 1 x10^2
- Fish CF 1 x 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)
- Commited effective dose per unit intake (Sv/Bq)
  ^{99}Tc - 6.4 x 10^{-10} (^{137}Cs - 1.3 x 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

<u>Day 1</u>

Seawater sample filtered

50 or 100 l samples

<u>Day 2</u>

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

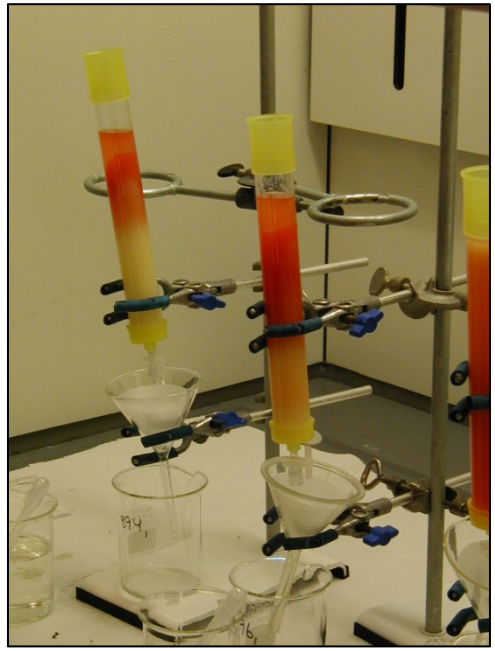
Day 3

Column washed (removes Ru isotopes)

- 100 ml H_2O
- 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_2O
- 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_2SO_4
- Add 19 ml H_2O
- Add 2 ml 15% NaClO. Heat for 10 minutes
- Add 40 ml H_2O
- 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 H_2SO_4
- Add 2 g $K_2S_2O_8$
- Bring to approx. 100 ml with H_2O
- Add 80 ml 5% Tri-isooctylamine in xylene - Shake 10 mins
- Discard aqueous phase
- Add 80 mls H_2O - Shake 5 mins.
- Discard aqueous phase
- Add 80 mls H_2O. Shake 5 mins.
- Discard aqueous phase
- Add 20 mls 2 M NaOH. Shake 2 mins.
- Collect aqueous phase
- Add 5 mls 0.5 M 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}Tc by NRPA

<u>Day 3 (continued)</u>

Electrodeposition on to steel planchettes

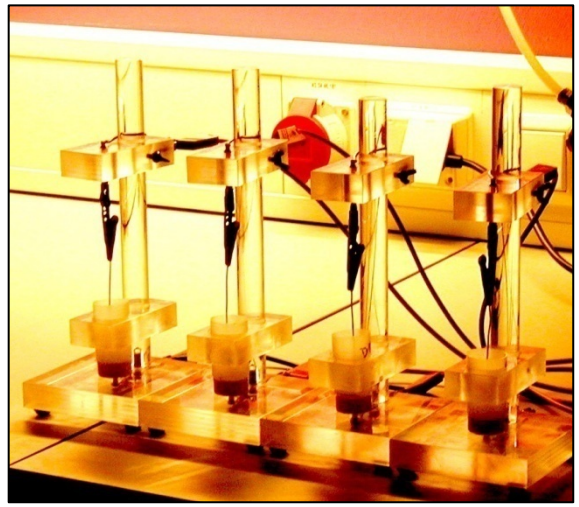
- 300 mA - 12 hours

<u>Day 4</u>

- Determine yield - gamma (^{99m}Tc)
- Planchettes packed for beta counting

<u>Beta Counting</u>

- 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…

^{99}Mo/^{99m}Tc generators

- ^{99m}Tc obtained from ^{99}Mo/^{99m}Tc generators
- Produced for hospitals - ^{99m}Tc nuclear imaging
- Readily available - relatively cheap to use
- ^{99}Mo loaded onto alumina column - irradiated Mo
- ^{99m}Tc (as TcO^{4-}) eluated out using a 0.9% NaCl solution
- Produced with a range of initial activities

<u>Tromsø</u>

- 20 to 30 GBq to hospital
- ~100 MBq when taken to laboratory
- 20-30 kBq ^{99m}Tc per sample
- <0.1 mBq of ^{99}Tc from decay of ^{99m}Tc
- Neglible 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.

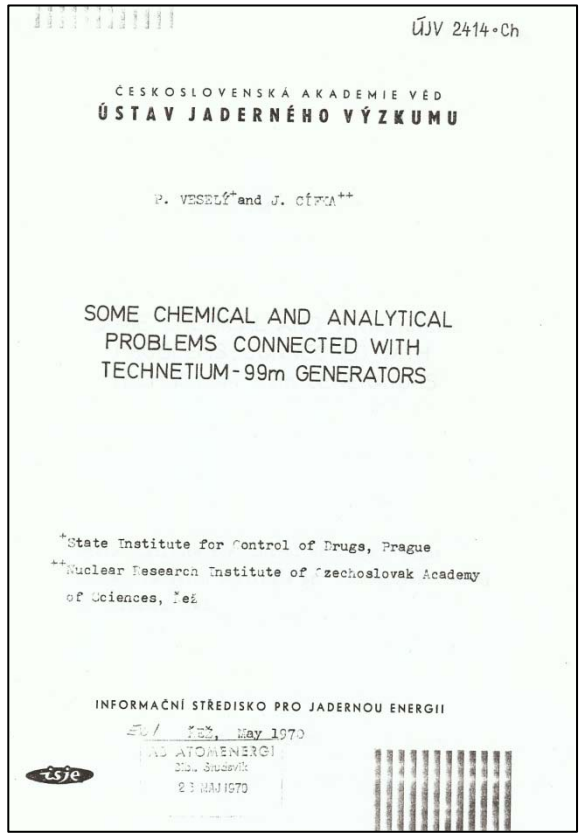
Possible contaminating radionuclides:

^{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!



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ČESKOSLOVENSKÁ AKADEMIE VĚD
ÚSTAV JADERNÉHO VÝZKUMU

P. VESELÝ[+] and J. ČÍPKA[++]

SOME CHEMICAL AND ANALYTICAL PROBLEMS CONNECTED WITH TECHNETIUM-99m GENERATORS

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[++]Nuclear Research Institute of Czechoslovak Academy of Sciences, Řež

INFORMAČNÍ STŘEDISKO PRO JADERNOU ENERGII

Řež, May 1970

ÚSTAV ATOMENERGIE
Dok. Studovník
23 MAJ 1970

From 1970

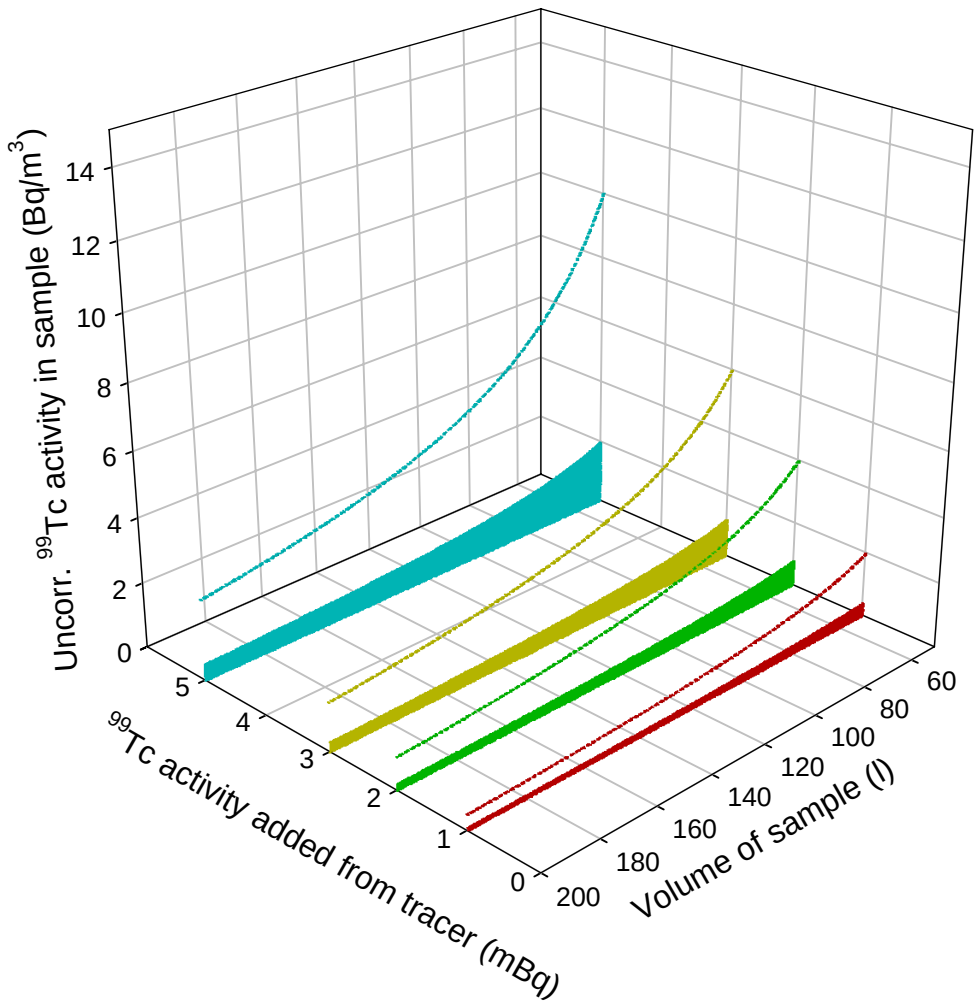
Breakthrough of ^{99}Tc…

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)

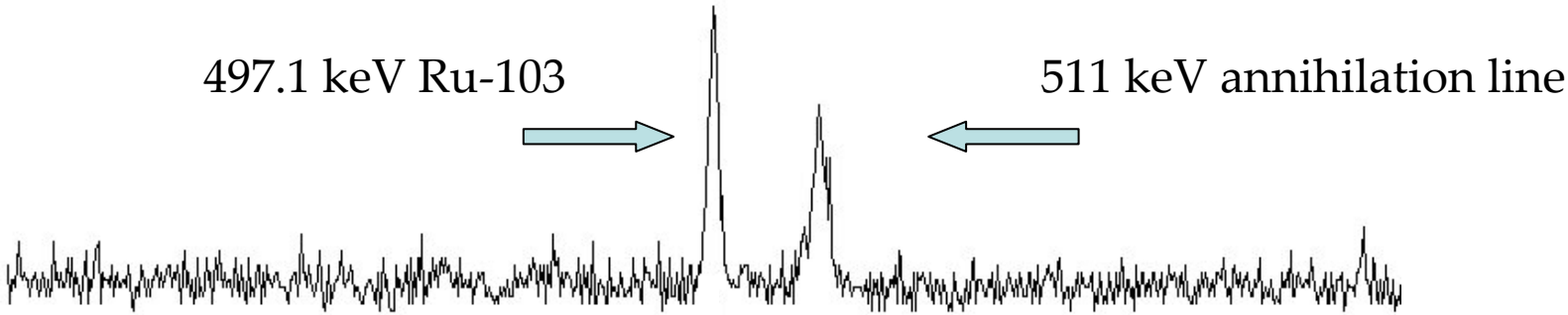
- Compared actual ratios of (moles total Tc/mCi ^{99m}Tc) versus theorectical calculations (based on initial activity and eluation history)
- Theorectical values underestimated the mass of total Tc by 25-300%
- Partly due to assumption in theorectical calculations that 100% of ^{99m}Tc is eluated
- Not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

- Theorectical 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

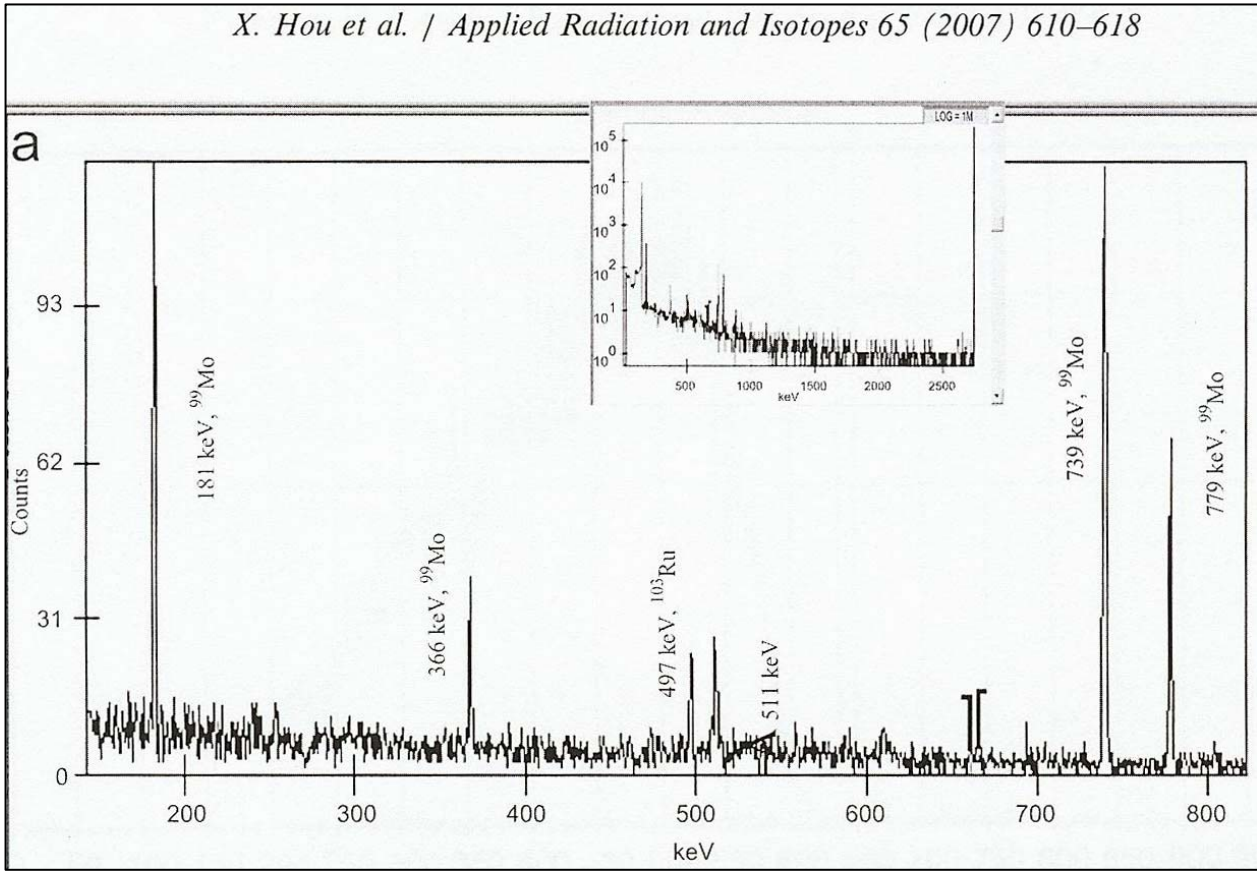


- No ^{99}Mo lines seen in this test…

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…

^{99}Tc activity (Bq/m^3) No correction	^{99}Tc activity (Bq/m^3) With correction
0.26 ± 0.03	0.25 ± 0.03
0.26 ± 0.03	0.23 ± 0.03
0.10 ± 0.01	0.08 ± 0.01
0.30 ± 0.03	0.24 ± 0.04
0.05 ± 0.01	< 0.05
0.28 ± 0.03	0.20 ± 0.04
0.12 ± 0.01	0.08 ± 0.02
0.31 ± 0.03	0.27 ± 0.04
0.10 ± 0.01	0.08 ± 0.01
0.30 ± 0.03	0.26 ± 0.04
0.29 ± 0.03	0.25 ± 0.04
0.18 ± 0.02	0.14 ± 0.03

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)

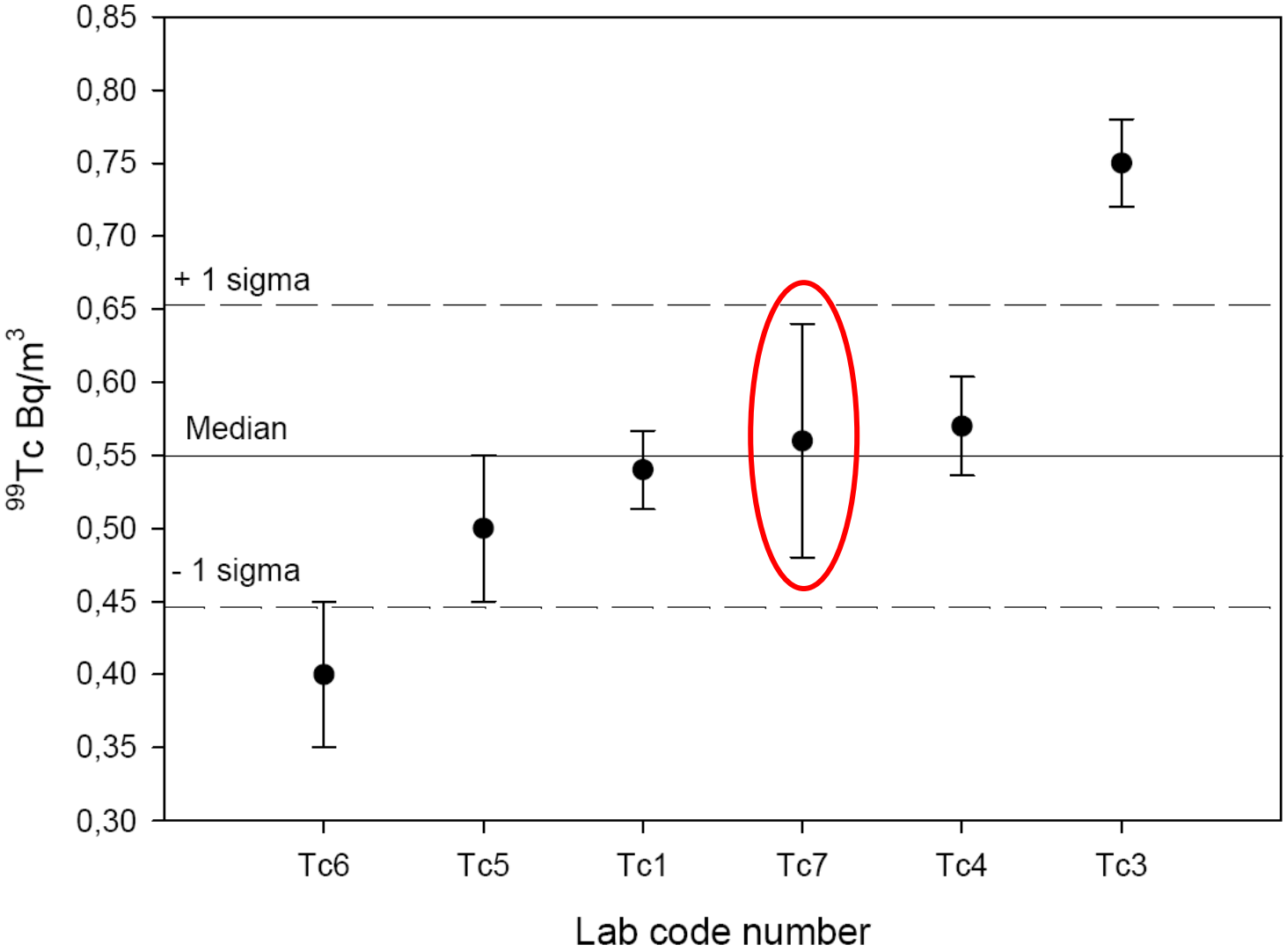
- Either by TEVA chromatography
- Or with Alumina cartridge filtration (x2)
- Both methods remove ^{99}Tc and ^{99}Mo
- Alumina cartridge easier and quicker to use - important due to high dose rates from ^{99m}Tc…
- No need to correct for contribution of ^{99}Tc from tracer
- Practical advice: always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

Volume (l)	^{99}Tc (Bq/m)^3
175	0.0571
176	0.0502
200	0.0458
200	0.0572
200	0.0264
186	0.0263
200	0.0476

Seawater from Greenland
5-10 mBq per sample

NRPA ^{99}Tc intercomparison - 2005

Low level seawater sample…



In conclusion…

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

Dowdall, M., Selnæs, Ø, Gwynn, J. and Lind, B. (2004). On the use of ^{99}Mo/^{99m}Tc generators in the analysis of low levels of ^{99}Tc in environmental samples by radiochemical methods. Water, Air, and Soil Pollution, 156: 287-297.

Hou, X., Jensen, M. and Nielsen, S.P. (2007). Use of ^{99m}Tc from a commercial ^{99}Mo/^{99m}Tc generator as yield tracer for the determination of ^{99}Tc at low levels