Physical Characterization of filters from German and Sweden radiological monitoring networks with ^{106}Ru from 2017

Health Canada

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Summary

- In late September to early October 2017, several national radiation surveillance networks in Eastern and Western Europe reported low levels of the airborne radionuclide contaminants ^{106}Ru and ^{103}Ru.

- Filters from the national networks of Sweden operated by the Swedish Defence Research Agency Totalförsvarets forskningsinstitut (FOI) and of Germany operated by the German meteorological services Deutscher Wetterdienst (DWD) containing ^{106}Ru were characterized physically including:

  - coincident gamma high resolution gamma spectroscopy
  - electron microscopy (not discussed here)
  - Autoradiography
  - Radiochemistry and reactivity studies

Objectives

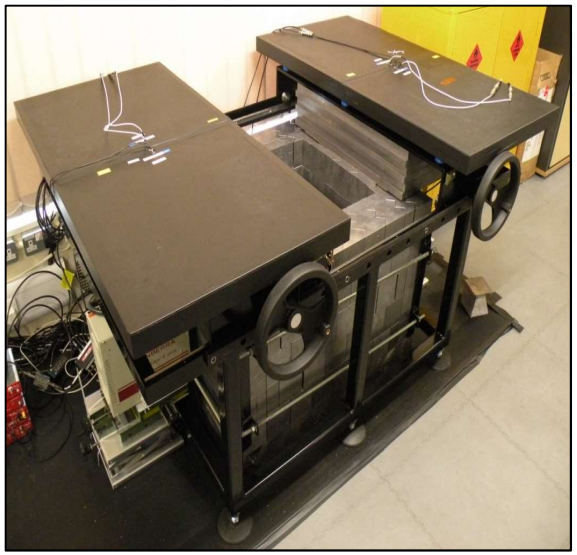
- Characterise Ruthenium on the filters in a way that:
  - Identify or limit the possible Ruthenium species and other nuclides on the filters.
  - Identify or limit the physical state of the Ruthenium on the filters and at the time of the dispersal incident
  - Use this to infer or limit the physical description of the ruthenium at the time of the dispersal incident

AWE

GAMMA RAY SPECTROSCOPY

$\gamma - \gamma$ Coincidence Spectrometry

- Dual Canberra BEGe 6530 plus veto
- Time-synchronised Canberra Lynx digital MCAs
- Time-stamped list-mode (TLIST) acquisitions
- Off-line data processing in ROOT
- Analysis of $\gamma - \gamma$ peaks in coincidence matrix



Results – Singles (DWD filter)

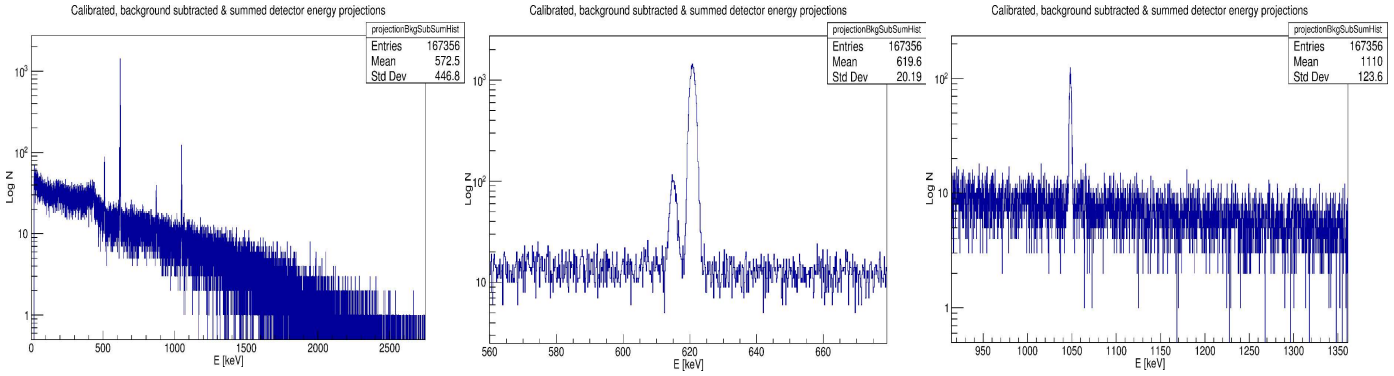
- Concentrations corrected to 2018/03/28 10:47 UTC (acquisition start)
- Count time 2.4×10^6 seconds in list mode
- Data sorted, histograms and coincidence matrices built using custom C++ / ROOT software
- Histograms analysed using Genie2K

Nuclide	DET-144 Bq/m3	+/-	DET-145 Bq/m3	+/-	Average Bq/m3
BE-7	3.42E-04	1.55E-05	3.13E-04	1.38E-05	3.28E-04
PB-210	6.84E-04	3.63E-05	6.52E-04	3.46E-05	6.68E-04
RH-106	7.04E-04	3.28E-05	6.48E-04	3.02E-05	6.76E-04

- Sample slightly off centre hence deviation between both detectors
- Average / combined result consistent with CAL05 analysis when corrected to collection start

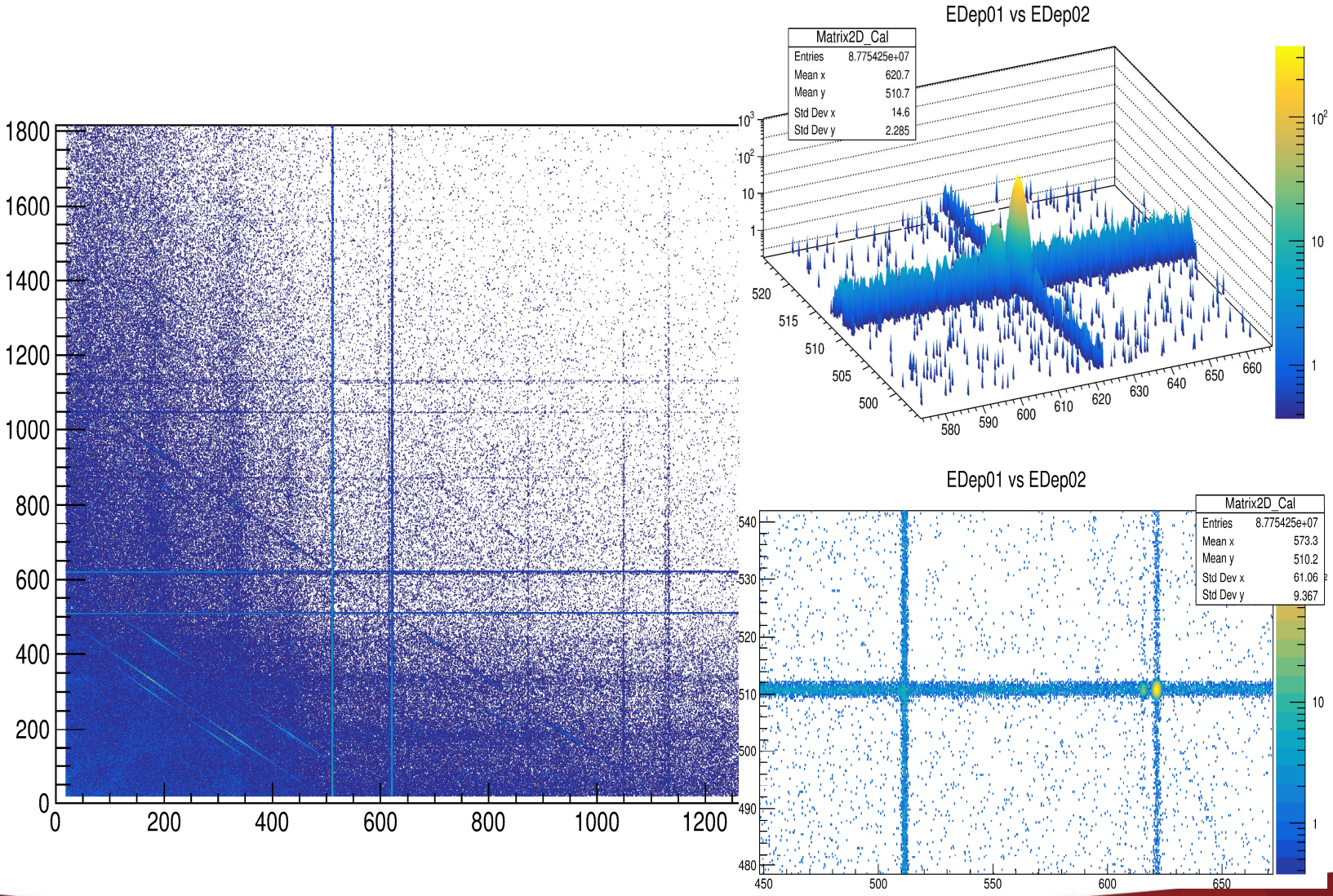
Results – Coincidence ^{106}Ru

Gate Energy	Projected Peak	RIMMER Factor	Area	cps	Bq	Bq/m3
511.861	621.93	3.79E-04	16672	0.006855	1.81E+01	7.17E-04
511.861	1050.41	3.68E-05	1514	0.000623	1.69E+01	6.72E-04
511.861	616.22	2.61E-05	1120	0.000461	1.77E+01	7.01E-04
616.22	873.49	4.89E-06	188	7.73E-05	1.58E+01	6.28E-04



- Sample slightly off centre hence slight deviation from singles data
- Consistency between four coincidence pairs gives high confidence in method

Results – Coincidence ^{106}Ru



Results – Singles and Coincidence MDAs

Nuclide	Singles MDA Bq/m3	Gate Energy	Projected Peak	RIMMER Factor	Backgorund Counts (projected)	Lc Currie	Lc Poisson	Coincidence MDA Bq/m3	Ratio to singles
CS-134	3.38E-07	604.721	796.00	2.02E-03	2	9	6	4.85E-08	0.143
BA-133	4.41E-07	30.625	356.00	7.10E-01	54	37	49	8.48E-10	0.002
AG-108m	4.76E-07	24.013	434.00	2.37E-04	61	39	75	2.69E-06	5.646
CO-60	5.14E-07	1173.23	1332.00	8.73E-04	1	7	3	5.61E-08	0.109
AG-110m	4.33E-07	657.76	885.00	1.04E-03	3	11	7	1.10E-07	0.254
EU-152	8.23E-07	40.118	245.00	2.08E-02	40	32	52	2.52E-08	0.031
SB-125	1.99E-06	27.202	408.00	9.01E-03	34	30	45	5.40E-08	0.027
SC-46	4.71E-07	889.277	1120.00	1.31E-03	1	7	3	3.74E-08	0.079
RH-102	1.08E-06	21.836	475.00	1.64E-04	30	28	41	2.80E-06	2.597
FE-59	9.00E-07	192.343	1100.00	1.81E-04	9	17	16	1.44E-06	1.603
LA-140	1.15E-06	328.762	487.00	1.08E-03	11	18	18	2.72E-07	0.237
CS-136	1.30E-06	31.817	1240.00	1.82E-03	7	15	13	1.17E-07	0.090
SB-126	1.01E-06	414.7	666.00	1.81E-03	5	13	10	9.02E-08	0.089
CE-144	8.57E-07	33.57	40.98	6.49E-05	21	24	11	6.04E-06	7.048

Background in some regions < 2 counts after 2.4×10^6 seconds (giving MDAs of the order ~nBq)

Conclusions Gamma Spectroscopy

- Material is very radio-pure
- The Ruthenium had an activity of 100 to 10000 times greater than other radionuclides considered.
- Any ^{144}Ce present had to be 1000 times less active than the released Ruthenium

HC

AUTORADIOGRAPHY

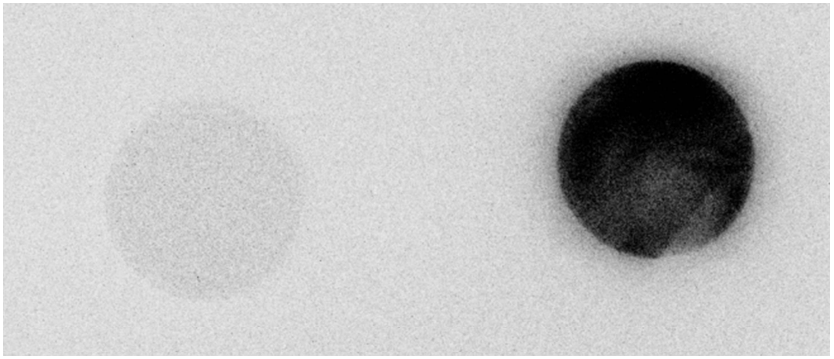
Results from BfS (DWD) Filter Measurement by HC

Activities decay corrected to 2018/02/09 20:24 UTC (sample acquisition date)

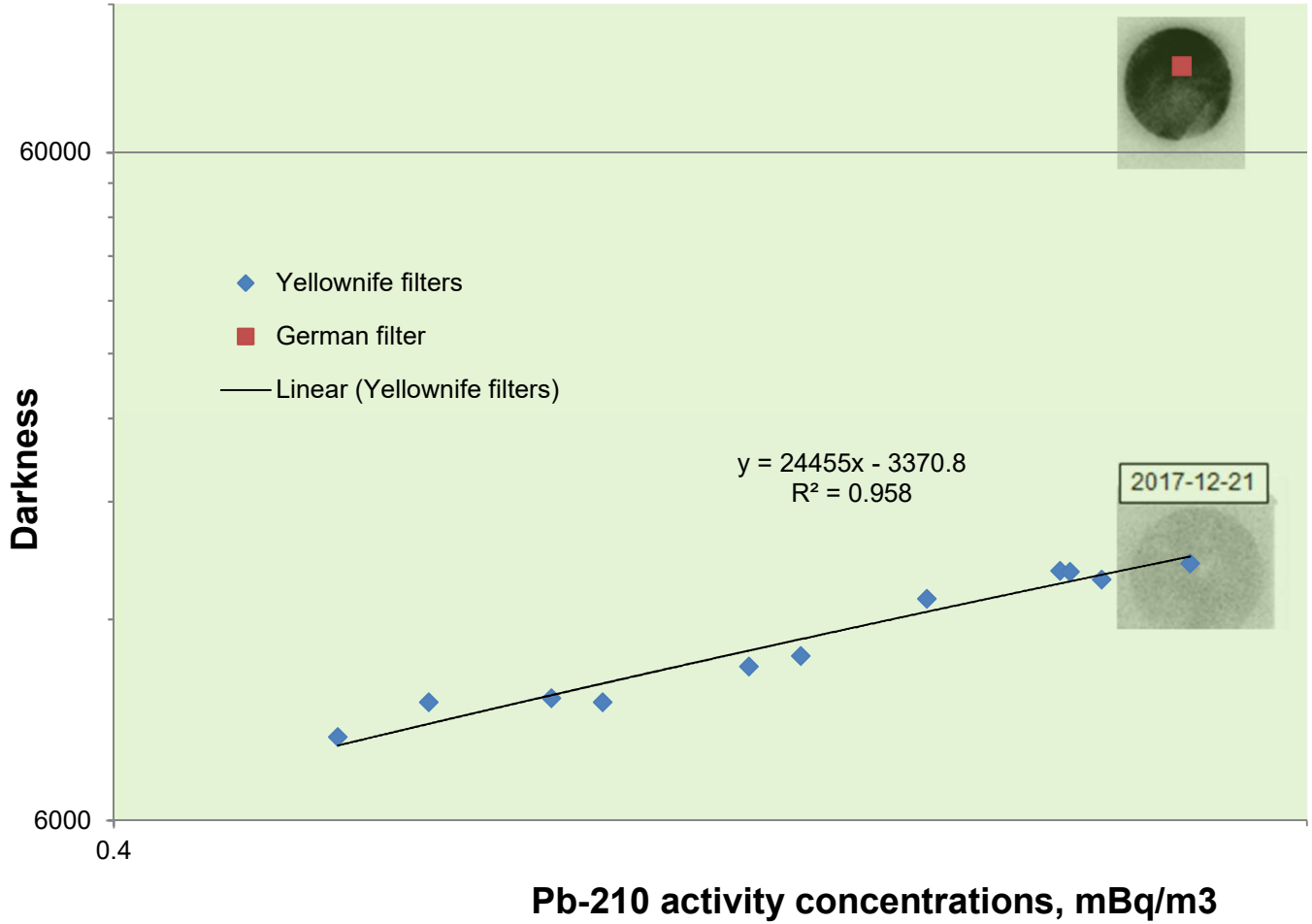
Concentrations corrected to 2017/09/25 12:00 UTC (collection start date)

- Collection was from 2017/09/25 to 2017/10/02 with a sample volume of 25194 m^3
- ^{106}Ru
  Activity = 18.7 Bq
  Concentration = 9.6×10^{-4} Bq/m^3
- ^{7}Be
  Activity = 11.4 Bq
  Concentration = 2.6×10^{-3} Bq/m^3
- ^{210}Pb
  Activity = 17.2 Bq
  Concentration = 6.9×10^{-4} Bq/m^3

Radiograph of Blank and Sample Filter



Ruthenium source of radiograph darkening



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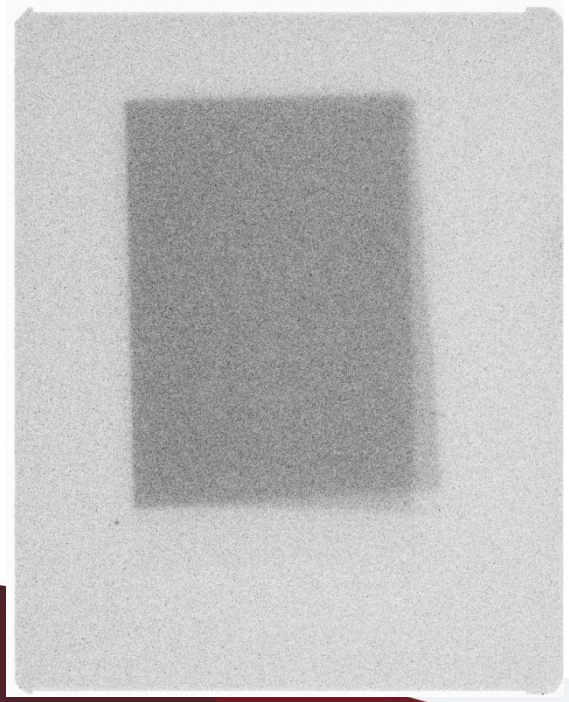
Filters From FOI

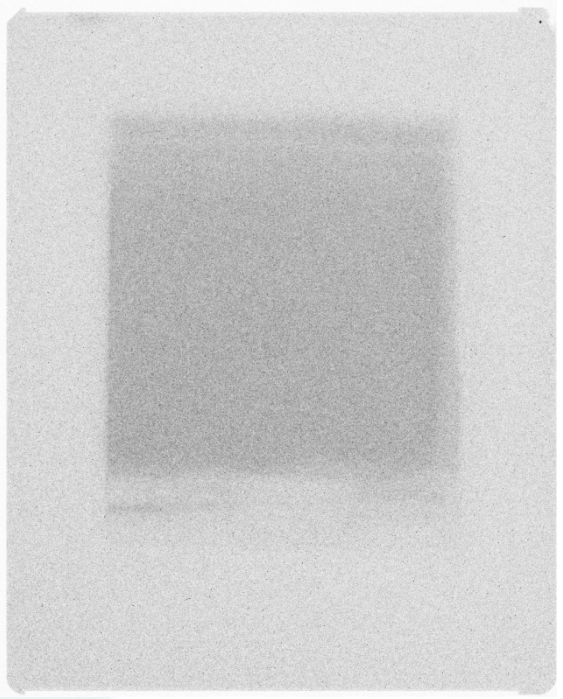
Canada

- FOI (Sweden) sent 6 filters, with 3 of them containing varying amounts of ^{106}Ru
- Each filter was radiographed.

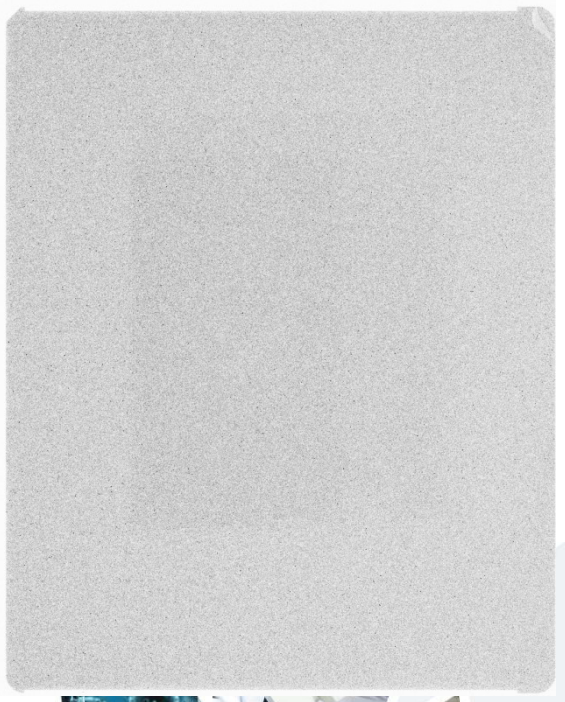
Gavle (50 Bq)



Visby (20 Bq)



Kiruna (1 Bq)



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Comments on Dispersion

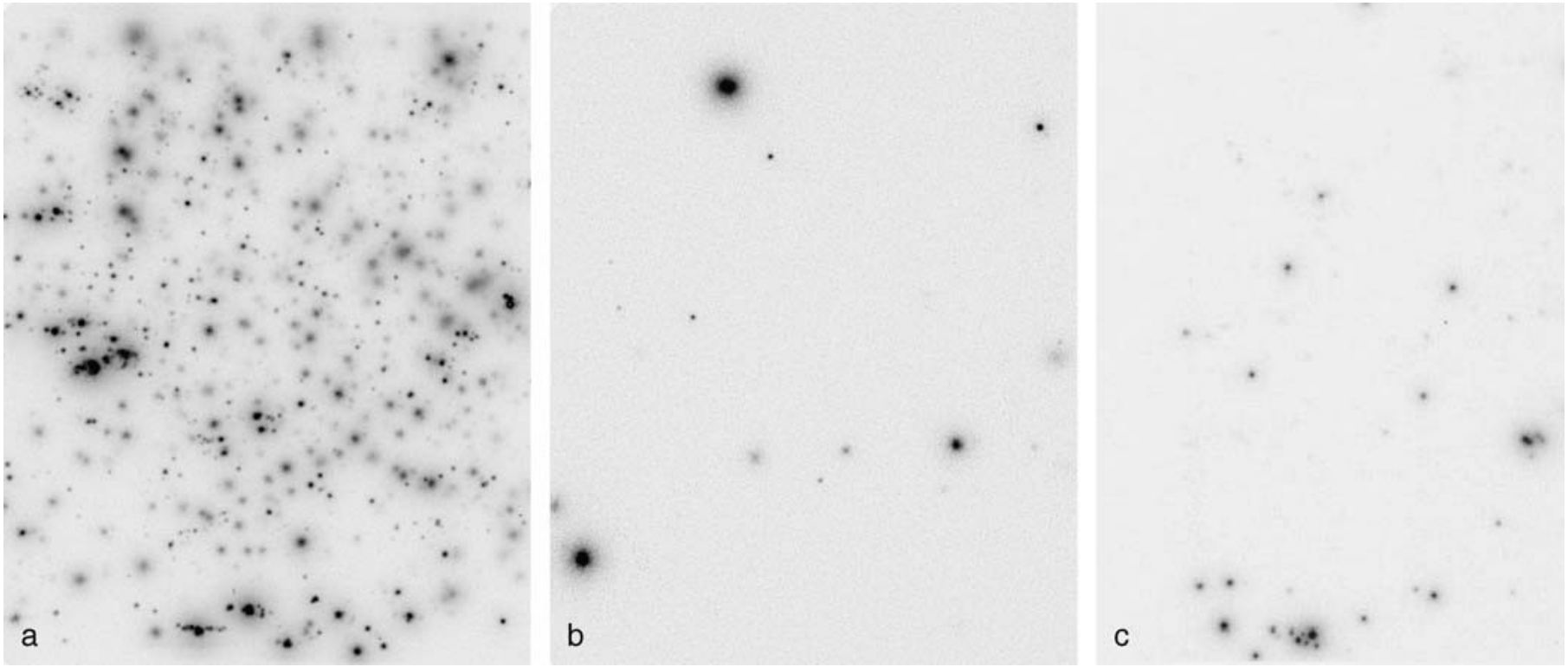
The DWD and FOI filters radiographs indicate the ruthenium is in a very highly dispersed form

The dispersion of the Ruthenium appears similar to the radon progeny ^{210}Pb, the only other contributor of significance to the radiograph image

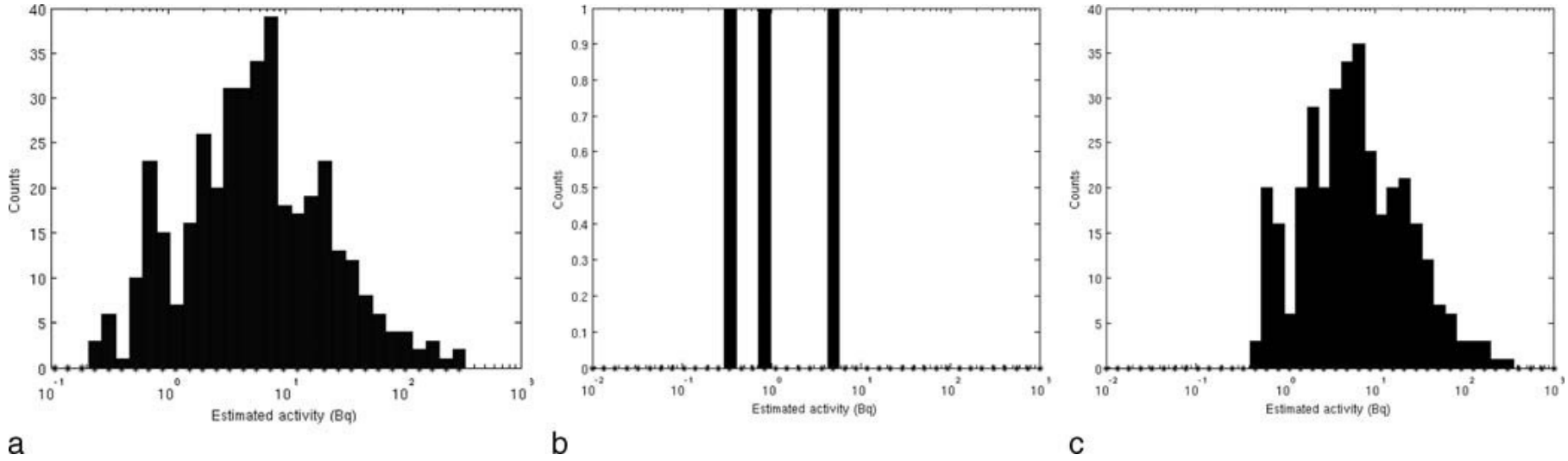
The size limits of the size of the domains of the Ruthenium may be limited by other radiography studies from a Canadian radioactive dispersal device (RDD) study* and filters from Takasaki after Fukushima.

*Particle Density Using Deposition Filters at the Full Scale RDD Experiments
May 2016,Health physics 110(5):471-480, Rodney Berg, Colleen Guihuly, Ed Korpach, Kurt Ungar

Images of filter laid on ground to capture deposits from Canadian RDD study*



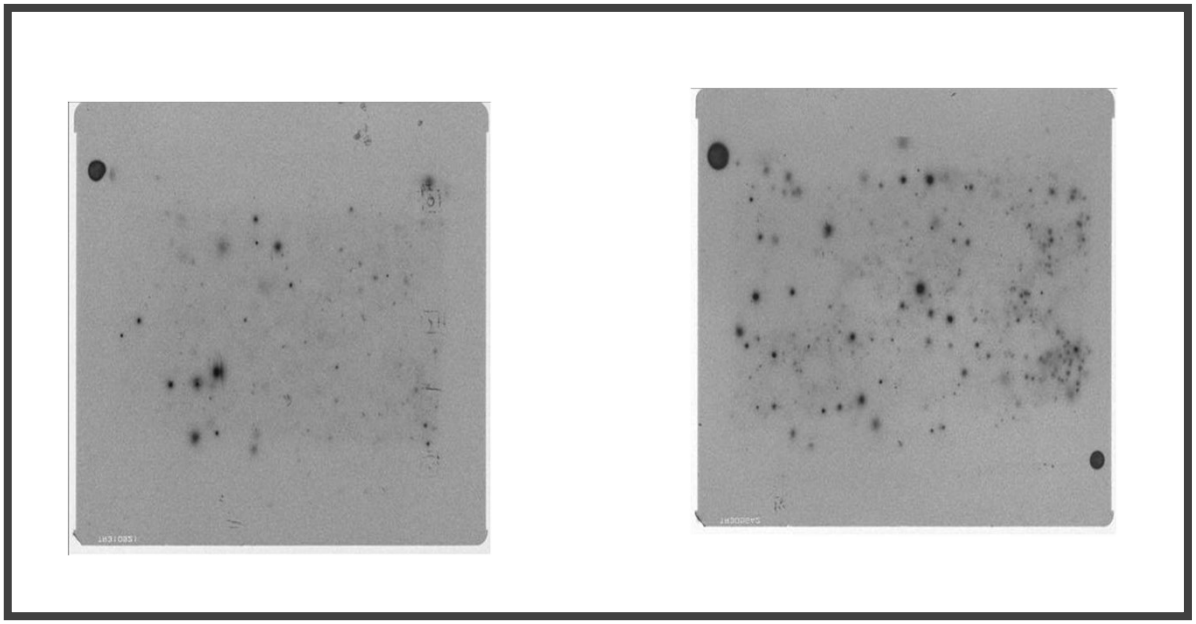
Detailed analysis of activity distribution of RDD particles



Represents $La(OH)_3$ particles ranging about 2 to 13 µm

Autoradiographs of the two Takasaki half RASA samples 3820110324 - March 24, 2011

- Note the bright, hot spots which demonstrate that most of the activity is contained in hot particles in a highly non-uniform distribution. Measured gamma activities of ^{134}Cs and ^{137}Cs on the right half are about a factor of 2 higher than the left half, corresponding to the difference in hot particle distribution



Comparison of radiographs and dispersion

- Takasaki radiographs appear similar to RDD in dispersion
- Samples taken at similar time in the region had particles in the 1 to 8 μm range*
- The domains of ruthenium likely are significantly smaller than 1 μm

*J Environ Radioact. 2014 Jun;132:1-7.
Size distribution of radioactive particles collected at Tokai, Japan 6 days after the nuclear accident.
Miyamoto Y[1], Yasuda K[2], Magara M[2].

"In the first collection, the activity median aerodynamic diameter (AMAD) of (134)Cs, (136)Cs and (137)Cs was 1.5-1.6 μm.The diameters of (134)Cs and (137)Cs in the second collection were expressed as three peaks at <0.5 μm, 0.94 μm, and 7.8 μm."

HC

RADIOCHEMISTRY

Model reactions

Chemical model reactions were performed to understand the species of Ru present

Reaction	Interpretation
Non-reactive and non-extractable component of activity	~25% of the ^{106}Ru on the filters exists as RuO_2
Ethanol extraction, reactivity studies	~ 1-2% of ^{106}Ru exists as β-$RuCl_3$
Reactivity studies and model reaction studies	The remainder of ^{106}Ru exists as a myriad of species (Ru^{7+} to Ru^{3+})
Insoluble in Carbon Tetrachloride	No RuO_4 present

Some Thoughts and Conclusions

- The ruthenium material was highly processed and radiopure with multiple species present, but no RuO_4.
- The original form was not likely pure RuO_2 as it is relatively inert and would not have readily converted into the different groups of species on the filter. Nanometer scale dispersion also would be difficult if it was dispersed in this pure form
- Ruthenium metal would be difficult to disperse without high temperature oxidation through RuO_4. Pure RuO_4 is very reactive but would not likely form the range of species on the filter without a relatively concentrated chemical environment. In a dilute environment, it would more likely convert to RuO_2. This cannot explain the soluble/reactive species on the filter but could lead to highly dispersed RuO_2
- RuO_4 is a common by-product in subsequent stages of purification in fuel reprocessing. It has a high vapour pressure and is readily dispersed. If the dispersal event included dispersion of other concentrated reagents and/or reaction products of RuO4, you could obtain a mixture of species released from the event site and at high dispersion on a final filter. No RuO_4 would be present on the filter in this case but RuO_2 product could be present as an insoluble portion. Other species would be present as well.

Building a better verification regime

CTBT verification requires non-destructive techniques. This scenario illustrated a few techniques not currently used in that could be valuable for CTBT

- γ- γ coincidence can provide greater sensitivity and certainty to identifications of many treaty relevant nuclides
- Autoradiography could provide the exact location of particles and then the specific location of activity could be measured in a well detector for much greater sensitivity

More certainty about absence of evidence and more certainty of evidence

– **Supports goal of verification regime to ensure no nuclear test goes undetected**

Thank You

BACKGROUND MATERIAL

Darkness of Filters-Is It Ruthenium?

Quantified radiograph images of the German sample + blanks and 11 Ru-free samples from Yellowknife station based on darkness of samples

- All areas, samples and background, were equal in size

Area of Darkness for German Filters (Background subtracted)

Blank = 3089
Sample = 83879

Darkness originates from ^{106}Ru and ^{210}Pb

Area of Darkness for Yellowknife samples (Background subtracted)

Sample Date	Area of Darkness
2017/12/21	14180
2017/12/22	12884
2017/12/23	14142
2017/12/24	10204
2017/12/25	13760
2017/12/26	8969
2017/12/27	9022
2017/12/28	8366
2017/12/29	9147
2017/12/30	10577
2017/12/31	12557

Darkness originates from ^{210}Pb

Compare [^{210}Pb] from Yellowknife stations

- Is there a correlation between amount of ^{210}Pb vs area of darkness?
- Compare to [^{210}Pb] from German sample

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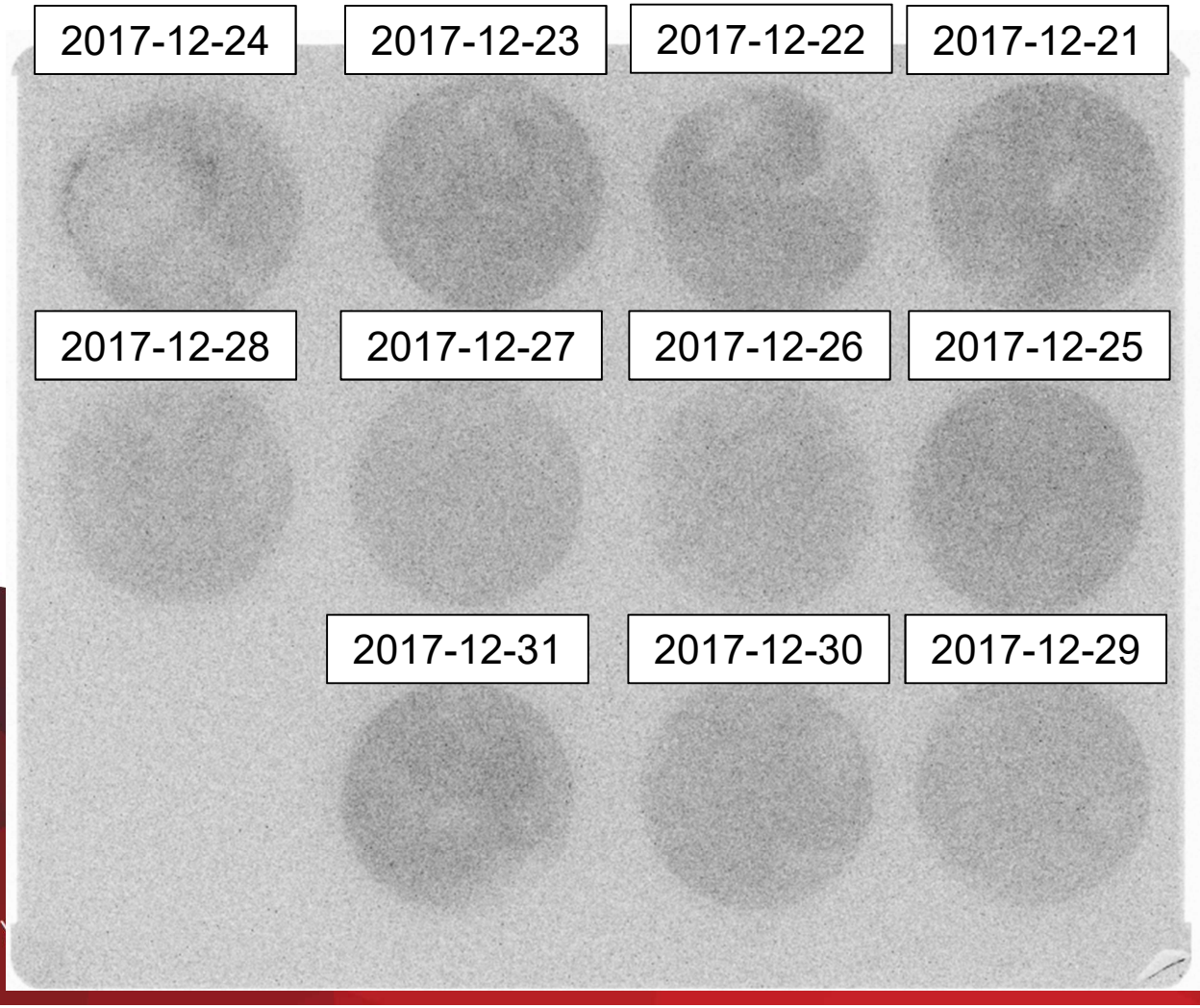
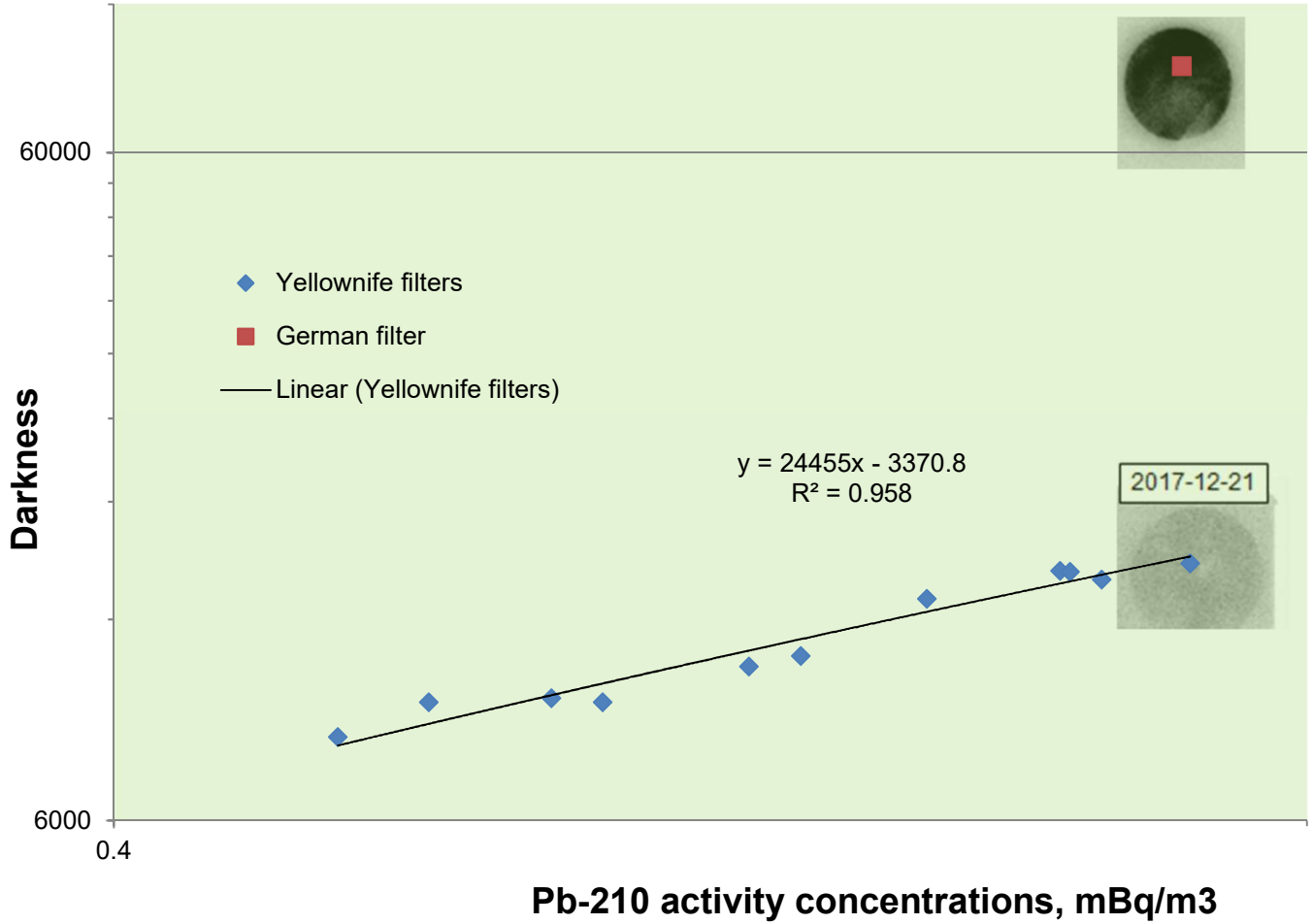
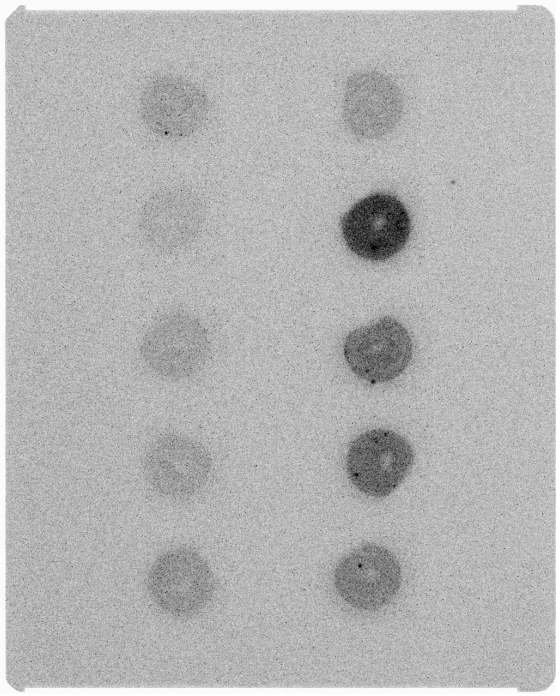
Baseline Radiograph of Samples from Yellowknife Station

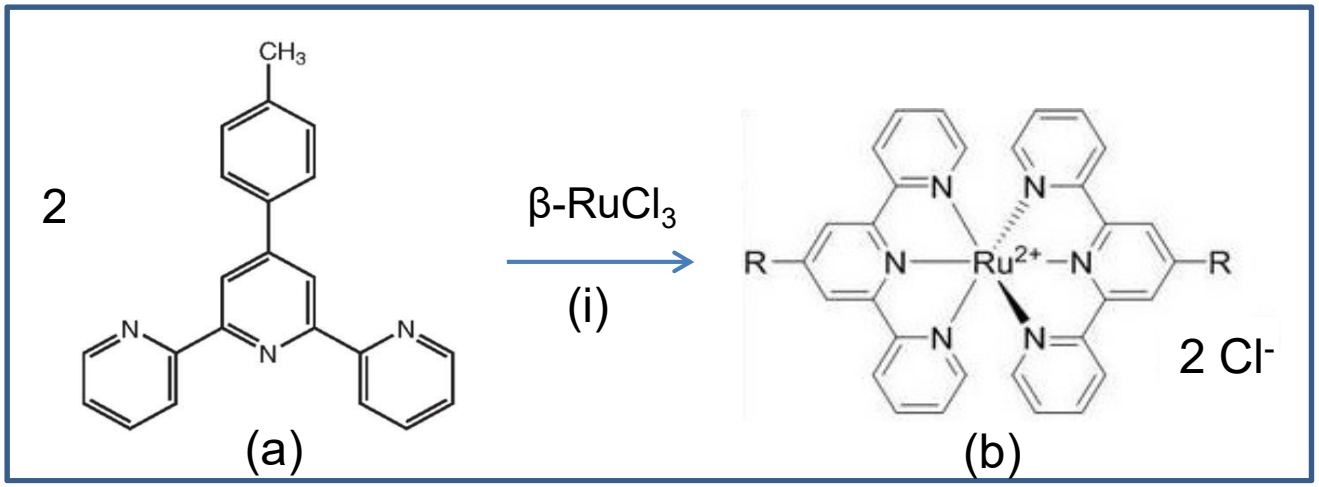


Ruthenium source of radiograph darkening

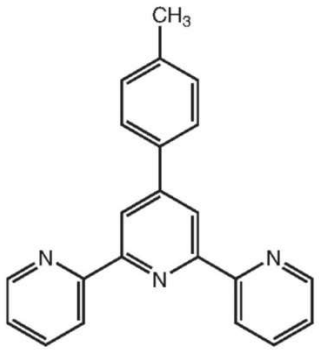




Chemical Transformations to Elucidate the Composition of Trace ^{106}Ru



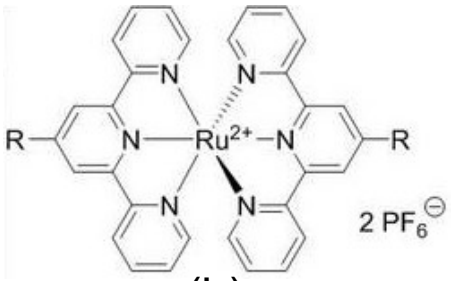
- The idea is to perform chemical reactions on ^{106}Ru in the presence of stable ruthenium and compare their respective fates
- If the reaction system is well-understood, in particular its limitations, we can make logical deductions about the native chemical form(s) of the ^{106}Ru contaminant
- Also serves to corroborate assessments based on solubility, since failures in particle filtration can masquerade as solubility (< 1 μm)
- Polypyridyl complexes of ruthenium (II) are exceptionally stable and intensely coloured (red), facilitating chromatographic purification
- Formed in high-yield in a reducing medium (e.g. ethanol) at elevated temperature from soluble Ru(III) halide salts, it is an attractive vehicle to assess the fate of ^{106}Ru compared to stable ruthenium
- Polypyridyl ligands based on 2,2';6',2"-terpyridine (e.g. (a), 4'-tolyl-terpyridine) are synthetically accessible and produce Ru(II) complexes in very high chemical yield



(a)

β-$RuCl_3$ + ^{106}Ru

1.) DMF/H_2O/Reflux
2.) 3 $AgNO_3$
3.) NH_4PF_6



(b)

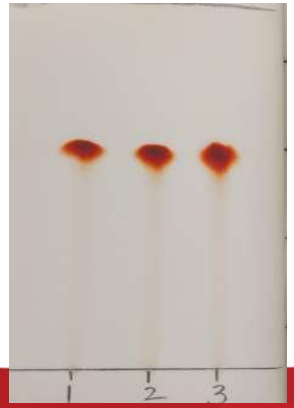
> 90% chem. yield

+ 3 $AgCl_{(s)}$

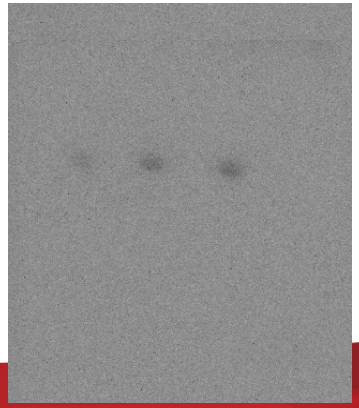
- A forceful application of the reaction was used, using N,N-dimethylformamide (DMF, b.p. = 153°C) and a dechlorinating agent (silver nitrate) at extended reaction times (18 h)
- The final product (b) is isolated by column chromotagraphy using silica as substrate and a mixture of acetonitrile and saturated aqueous potassium nitrate (7:1) as mobile phase
- Conversion to the more organic-soluble hexafluorophosphate salt of (b) was effected by precipitation in water and NH_4PF_6, followed by final precipitation in diethyl ether
- To demonstrate radio-purity and incorporation of ^{106}Ru into the final product, a radiograph is depicted below of reaction products from three reactions when eluted on a silica plate

Direction of mobile phase elution on silica plate

a

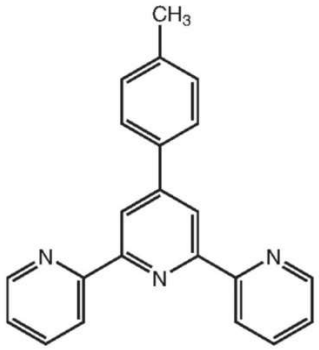


b



a = elution of $Ru(tolyl\text{- }tpy)_2](PF_6)_2$ on silica

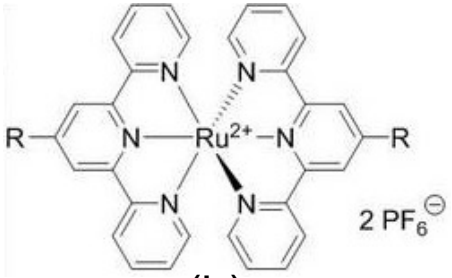
b = radiograph of eluted $Ru(tolyl\text{-}tpy)_2](PF_6)_2$ on silica



(a)

β-$RuCl_3$ + ^{106}Ru

1.) DMF/H_2O/Reflux
2.) 3 $AgNO_3$
3.) NH_4PF_6



(b)

> 90% chem. yield

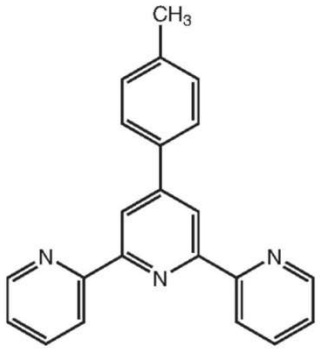
+ 3 $AgCl_{(s)}$

- When applied to a filter piece, 70 – 75 % of the activity was found to be incorporated into the final product (b) after isolation, with the balance distributed between the filter and silver choride. More resolution needed.

- 50 - 55% of the filter activity was found to be associated with water after a brief and gentle aqueous wash and ultra-filtration. The aqueous extract and remaining filter piece were reacted separately

  - It was found that almost all aqueous activity was isolated in complex (b) after reaction; however, only 56 % of activity remaining on the washed filter was incorporated into complex (b)

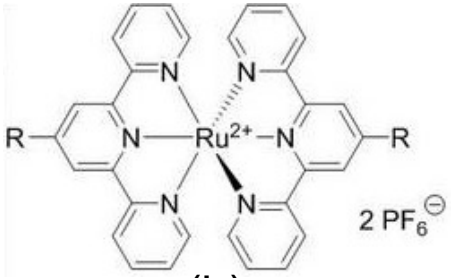
  - So what ruthenium species do not react under these conditions?



(a)

RuX_nY_m

1.) DMF/H_2O/Reflux
2.) 3 $AgNO_3$
3.) NH_4PF_6



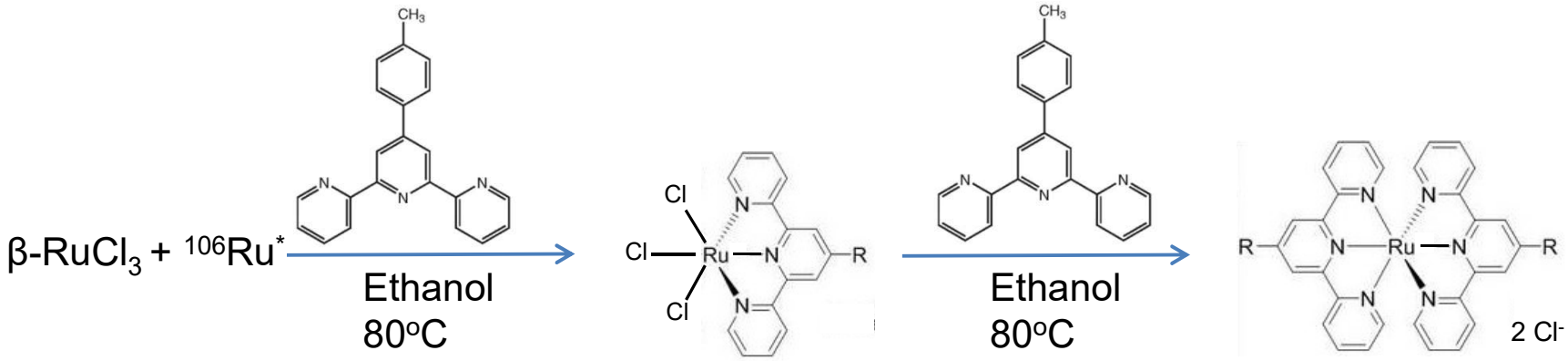
(b)

+ *n* $AgX_{(s)}$ + *m* Y

- The limitations of the reaction system were assessed against ruthenium compounds that are representative of species encountered in large-scale nuclear waste processing via the generation of the volatile $RuO_{4\ (g)}$ under harsh oxidative conditions. These are:

Compound	Result (chemical yield, %)
$(NH_4)_2RuCl_6$	90 – 95 %
$Ru(NO_3)_3(NO)$	92 %
$KRuO_4$	19 % (no reaction using ethanol)
RuO_2	no reaction

- Surprisingly, the reaction was found to be very general, accommodating even multi-electron reduction in the case of ruthenium (IV) and ruthenium (VII) salts (previously unknown)
- Note that $KRuO_4$ and its more reactive counterpart, K_2RuO_4, react with water (and other reducing solvents) to generate RuO_2
- RuO_2, a highly insoluble coordination polymer of Ru^{4+}, is completely non-reactive



activity from ethanol wash of filter

Ethanol Extraction/Reaction Details:

- < 10 % of ^{106}Ru on the filter is quickly extracted into ethanol
- β-$RuCl_3$ is highly soluble in ethanol – a relatively rare property amongst ruthenium salts
- The reaction to form (a) from β-$RuCl_3$ is mild and selective, involving no change in oxidation state of ruthenium, where the tolyl-terpyridine ligand simply displaces weakly bound water molecules
- The intermediate (a) is charge neutral and highly insoluble in ethanol

Observations:

- 35 – 40 % of the ^{106}Ru activity was isolated with complex (a)
- Complex (a) was then reacted further with near-quantitative incorporation of ^{106}Ru into complex (b)

Notes:

- Ligand-metal bonding (N-Ru) is possible only for relatively electron rich Ru (i.e. Ru^{3+} or Ru^{2+})
- Strong evidence to support the existence of β-$RuCl_3$ as a component to the ^{106}Ru contaminant (< 4%)

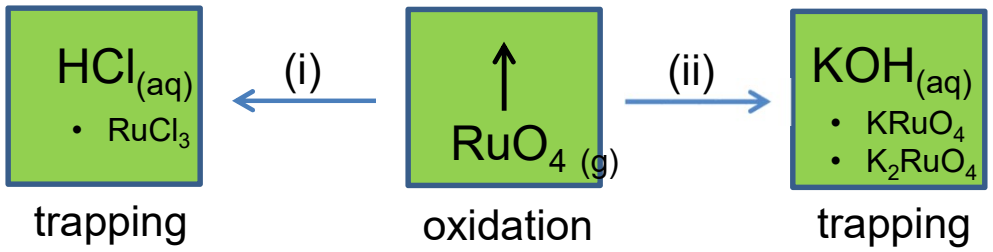
Tentative Conclusions:

It is likely that:

- ~ 25% of the ^{106}Ru on the filters exists as RuO_2
- The remainder of ^{106}Ru exists as a myriad of species (Ru^{7+} to Ru^{3+})
- A small (< 4%) proportion of ^{106}Ru exists as β-$RuCl_3$

Considering:

- Reductive trapping of RuO_4 vapour (generated upon oxidative treatment of nuclear waste) using vast amounts of hydrochloric acid (HCl) or potassium hydroxide (KOH) solutions is extremely practical
- $RuCl_3$ is a principle product of trapping with HCl, it is possible that ^{106}Ru release was associated with the initiation of this process



On-Going Work:

- Work is on-going to demonstrate the existence of β-$RuCl_3$ as a component of the ^{106}Ru contaminant, in the absence of added stable (carrier) ruthenium