Investigation of TBP resin for the separation and purification of polonium from bismuth target

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Why Polonium-210 ?

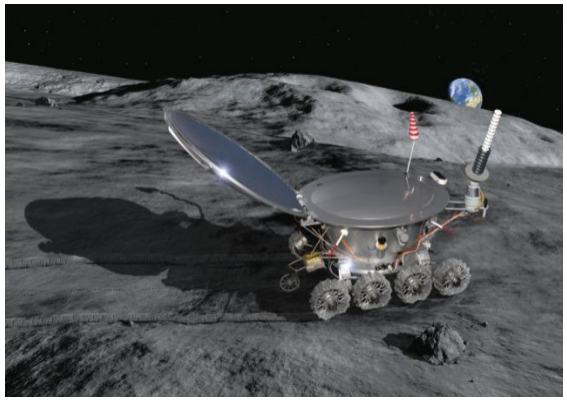
- Discovery was published in July 1898 by P. and M. Curie.
- Have a 138.46 days half-life
- 42 isotopes: ^{208}Po, ^{209}Po, ^{210}Po, ^{212}Po, ^{216}Po, ^{218}Po,… but all radioactive

Toxicity

Alexander Litvinenko (former Russian spy) poisoned by polonium-210 on Nov. 1 ,2006 and died 3 weeks later

LD_{50}= 1 µg in comparison to 250 milligram HCN

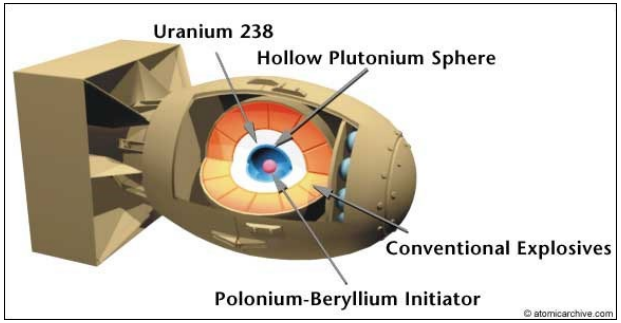
Space application



Radioisotopes thermoelectric generator as long terms power sources for unmanned devices (space probes and satellites).

Po= 140 W g^{-1} *vs.* ^{238}Pu = 0.54 W g^{-1}

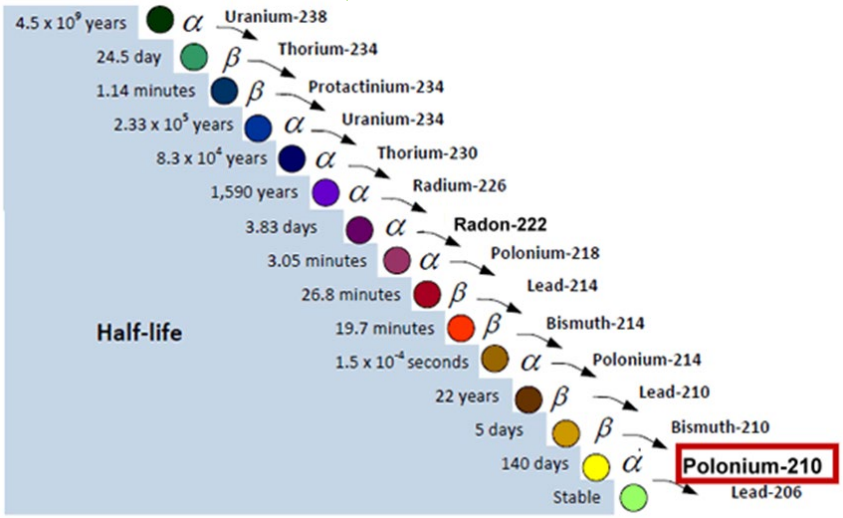
Military application



Fat man atomic nuclear bomb- dropped on Nagasaki

Production of Polonium-210

Natural production



$$^{210}_{82}Pb \xrightarrow[22.3\ years]{\beta} {}^{210}_{83}Bi \xrightarrow[5days]{\beta} {}^{210}_{84}Po$$

^{210}Po exists in uranium ores (0.1mg / ton)

Artificial production

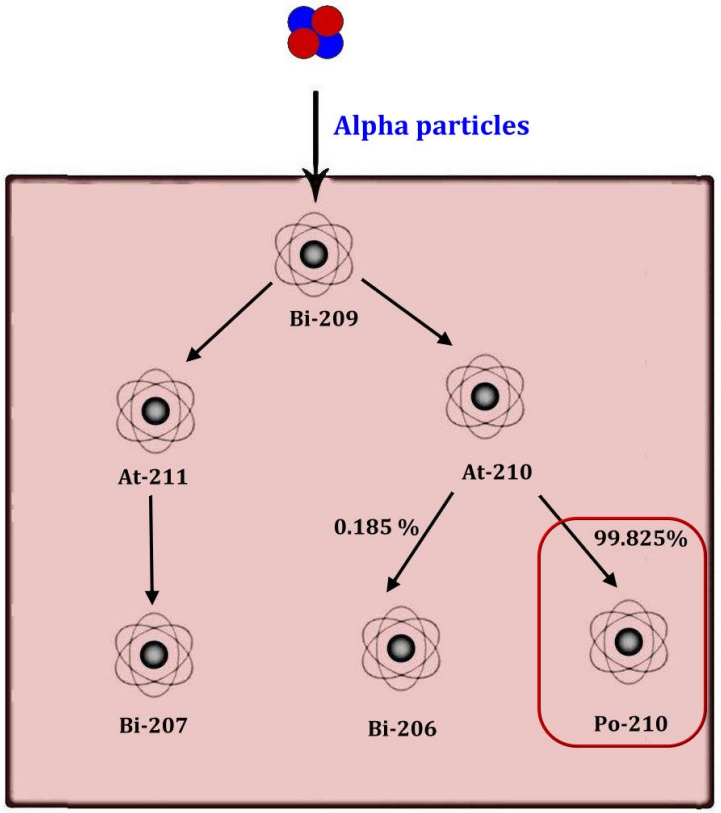
- **Neutron –irradiation**

$$^{209}_{83}Bi(n,\gamma)\ {}^{210}_{83}Bi \xrightarrow[5days]{\beta} {}^{210}_{84}Po$$

- **Deuterium –irradiation**

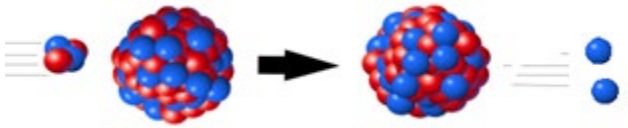
$$^{209}_{83}Bi + {}^{2}_{1}d \longrightarrow {}^{210}_{84}Po + {}^{1}_{0}n$$

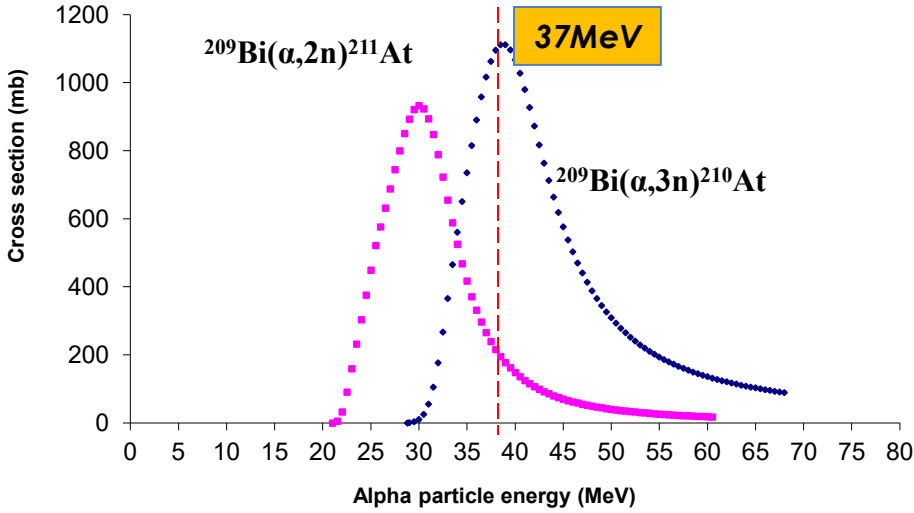
Production of Po with a cyclotron ?



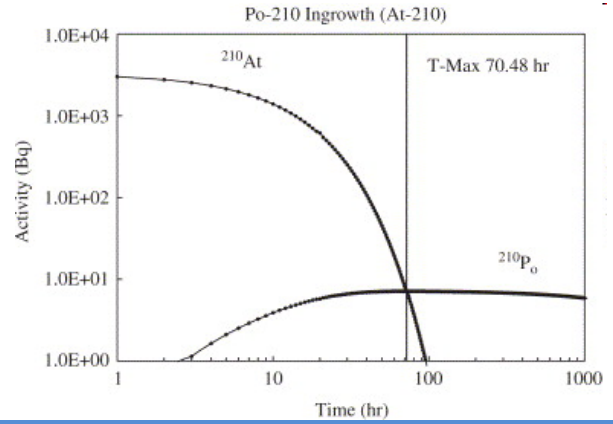
Decay of stable Bi-209 by alpha bombardment

$$^{209}_{83}Bi + ^{4}_{2}He \longrightarrow ^{3}_{0}n + ^{210}_{85}At \longrightarrow ^{210}_{84}Po + ^{206}_{83}Bi$$





Cross section data taken from the literature for the ^{209}Bi(α,2n)^{211}At and ^{209}Bi(α,3n)^{210}At reactions



The decay scheme of At-210 showing the maximum theoretical time for Po-210 production.(1)

1. M.K. Schultz et al. / Applied Radiation and Isotopes 64 (2006) 1365–1369..

Purification Method ?

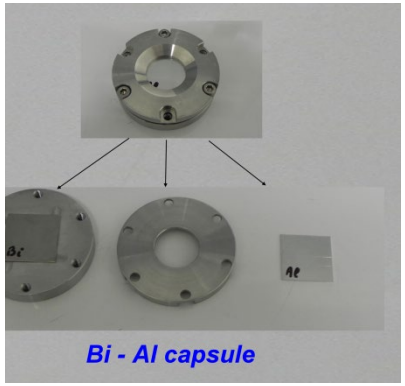
Irradiated Bi foil

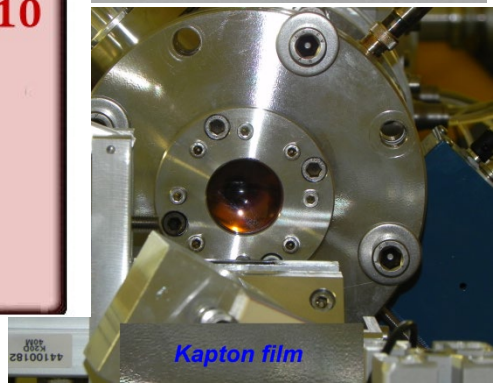
7 days

Macroscopic quantities Bi-209 (0.028 mol)

Radiotracer Po-210 ($2.6\ 10^{-13}$ mol)

Ratio 10^{11} : 1



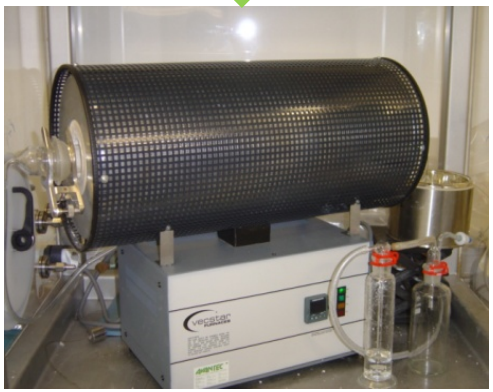


- A_{At-210} =4.11MBq
- A_{Po-210} =10KBq

- I= 0.2 µA -1 hr
- Bismuth-209 thickness 0.9 mm.
- Stopping point in Bi-209 : 327.42 µm

Po/ Bi Purification

Distillation (1)



1- Heat 600-650 °C /He flow.
2- Dissolve in HCl.
3- Spontaneous deposition on Ag or Pt.
4- Redissolved & precipitated as sulfied.

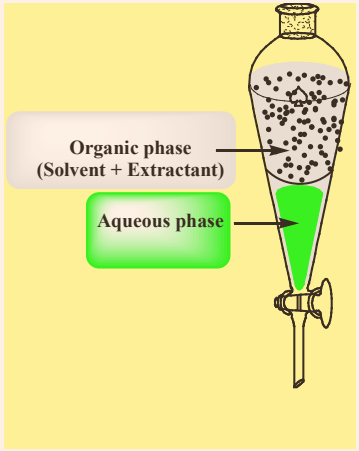
➢ Non-reproducible
➢ Po/Ag or Pt purification

Chromatography (2)

1- Elute Bi with 2M HCl.
2- Elute Po with 6M HNO_3 .

➢ Co- precipitation of Po/Bi
➢ tracer Po/Bi fraction

Solvent extraction (3)

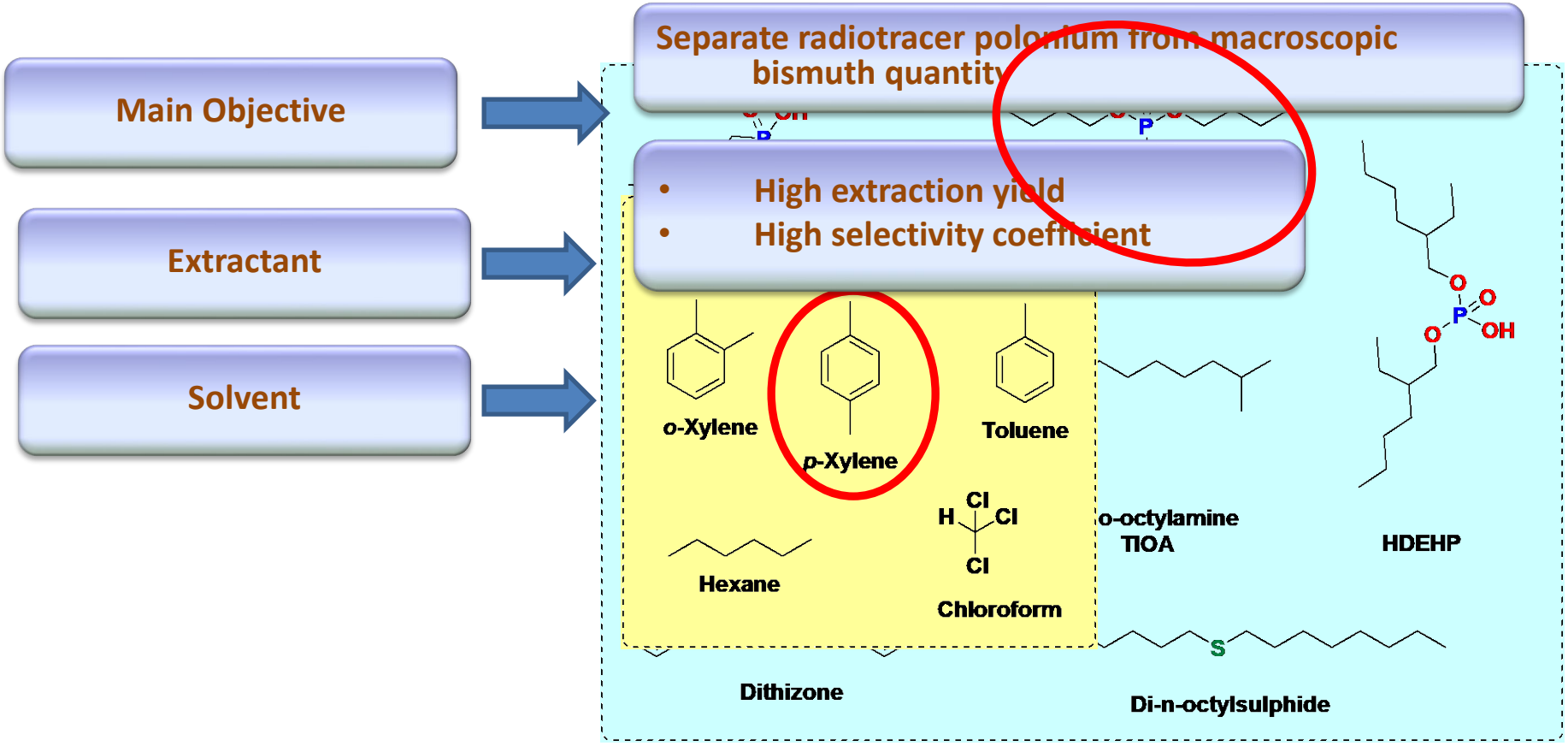


1- Po extracted to organic layer.
2- Bi remains in aqueous layer .
3- Extractant : TBP , TIOA,DDTC,…

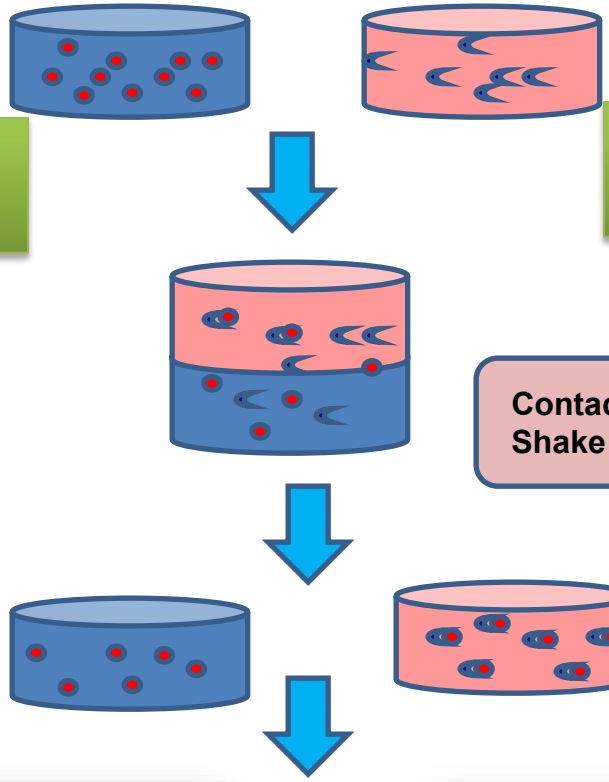
Extraction yield

1. M.B.Mikheev, "POLONIUM" ,Chemiker Zeitung, September 1978 ,(UCRL-Trans—12034).
2. N.Vajda .J.Environ.Radioactivity, Vol.37 , No.3 , pp.355-372, 1997.
3. Y. M. CHEN AND R. Y. SHU.J.Chin.Chem.Soc.(Taiwan),13;82-95(June 1966).

Solvent extraction



1. Chen. YM., Shu, RY.: J. Chin. Chem. Soc. 13, 82-89 (1966).
2. Bagnell, K. W., Robertson, D. S.: Solvent extraction studies with polonium. J. Chem. Soc. 509-512 (1957).
3. Karracker, D. G., Templeton, D. H.:J. Phys. Rev. 81, 510 (1951).



Aqueous phase
^{210}Po/ Bi in HCl
or HNO_3

Pre- equilibrated
Organic phase
TBP in *para*-xylene

Contact &
Shake for time t

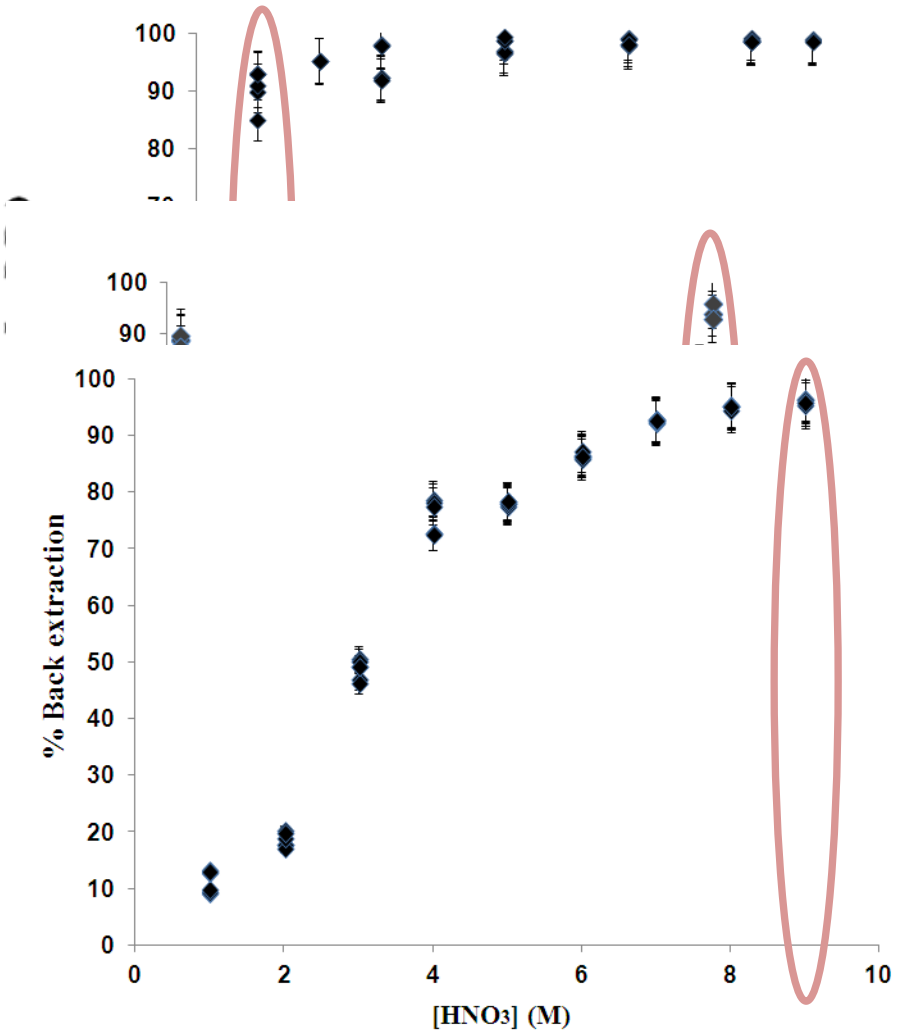
Separate both
phases

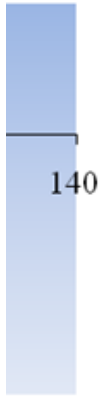
Measure aliquot using LSC and α-β
proportional counting

Solvent extraction

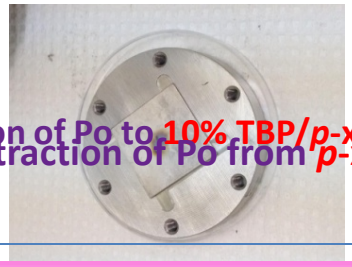
Batch studies

- Kinetics studies
- Influence of [TBP]
- Influence of [HCl]
- Influence of [HNO_3]



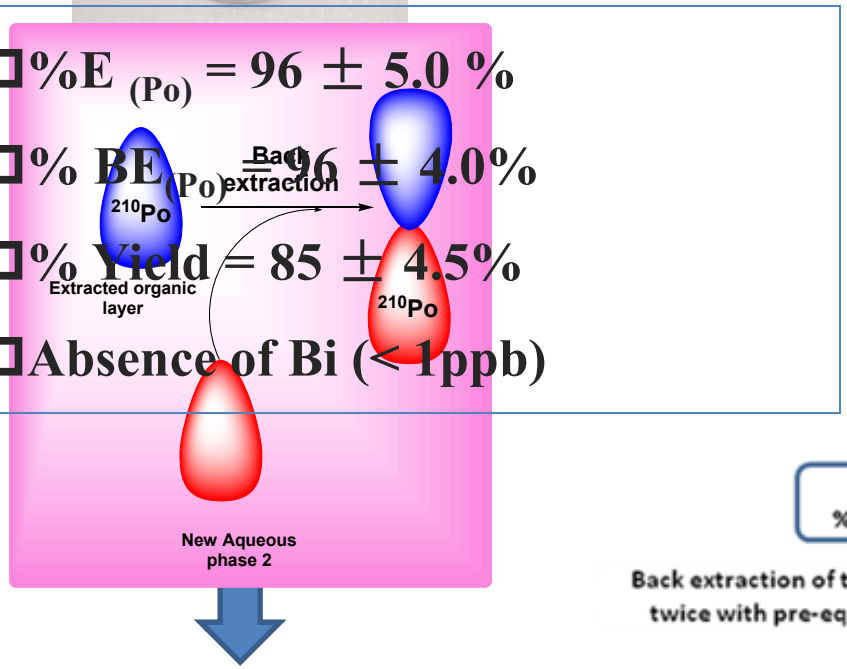


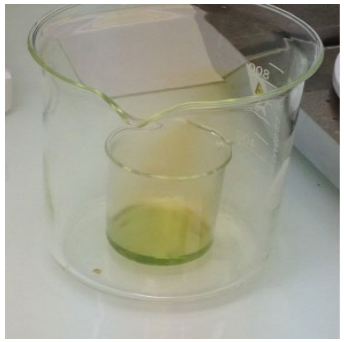
Real target



Extraction of Po to 10% TBP/*p*-xylene from 7M HCl
Back extraction of Po from *p*-xylene to 9M HNO_3

- $\%E_{(Po)} = 96 \pm 5.0\ \%$
- $\%\ BE_{(Po)} = 96 \pm 4.0\%$
- $\%\ Yield = 85 \pm 4.5\%$
- Absence of Bi (< 1ppb)





Irradiated Bi-209 foil

Left for 7 days for At-210 decay

Dissolved in 22 ml (10M) HNO_3

Evaporated using IR lamp

Reconditioned in 55ml (7M) HCl after two evaporation cycles

Extraction in 10% TBP in *para*-xylene

V organic =V aqueous = 55 mL

Organic phase
% Po-210 > 96 ± 5%

Aqueous phase
% Bi > 99.3 ± 0.5%

Back extraction of the negligible extracted Bi by washing twice with pre-equilibrated aqueous phase of 7M HCl

Organic phase
% Po-210 > 96 ± 5%

Back extraction in 9M HNO_3

Total recovery yield of Po-210 = 85.2 ± 4.5%

Organic phase

Aqueous phase
% Po-210 > 96 ± 4%

Reconditioning

A. Younes et al. A route for polonium 210 production from alpha irradiated bismuth 209 target. Radiochimica. Acta. 102(8), 681-689, (2014).
A.Younes, et al, Solvent extraction of polonium (IV) with tributyl-phosphate (TBP). Journal of Solvent Extraction and Ion Exchange. 35(2), 77-90, (2017).

Green process ?? No organic solvent

TBP resin

Real target

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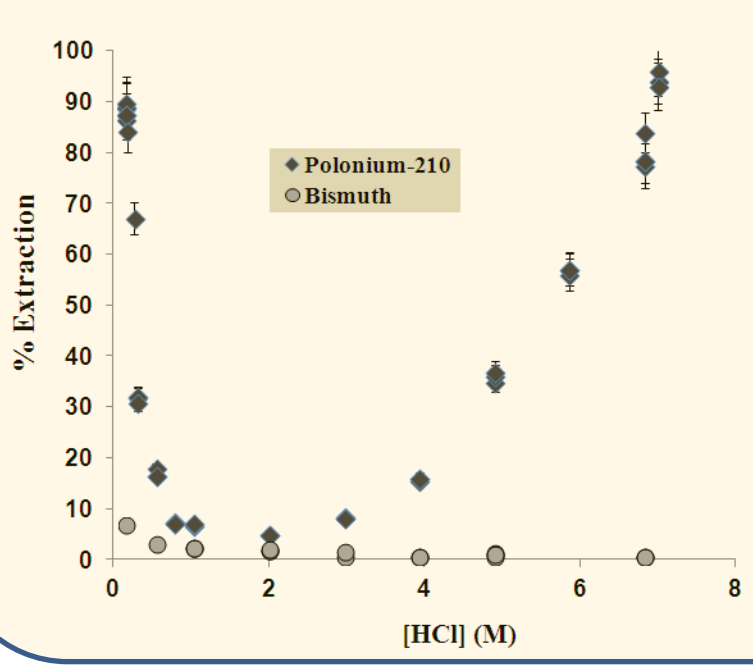
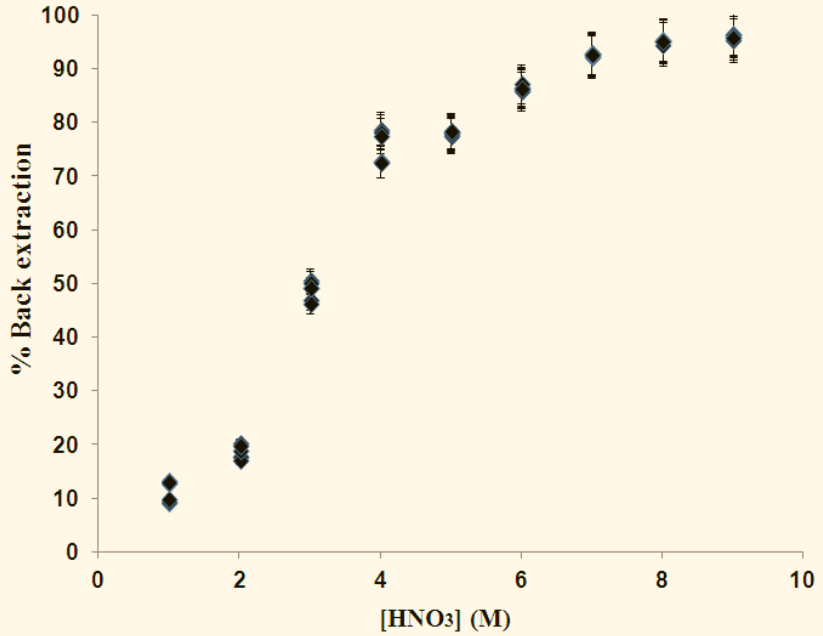
Po/ Bi Purification

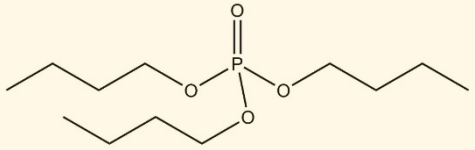




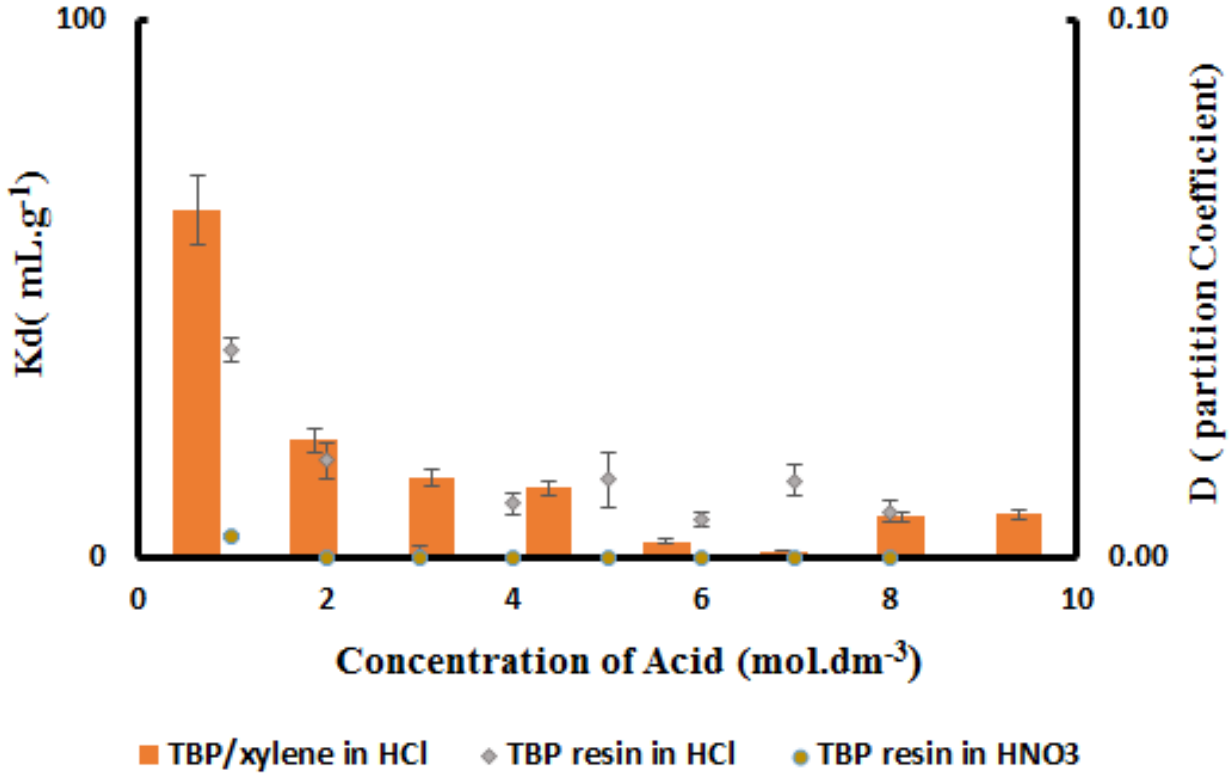
Solvent Extraction:

- **Po/Bi separation [HCl]>7 M**
- **Po/TBP [HNO_3]>7 M**

TBP resin binding site: 1.47 ± 0.08 mmol TBP per gram of resin.



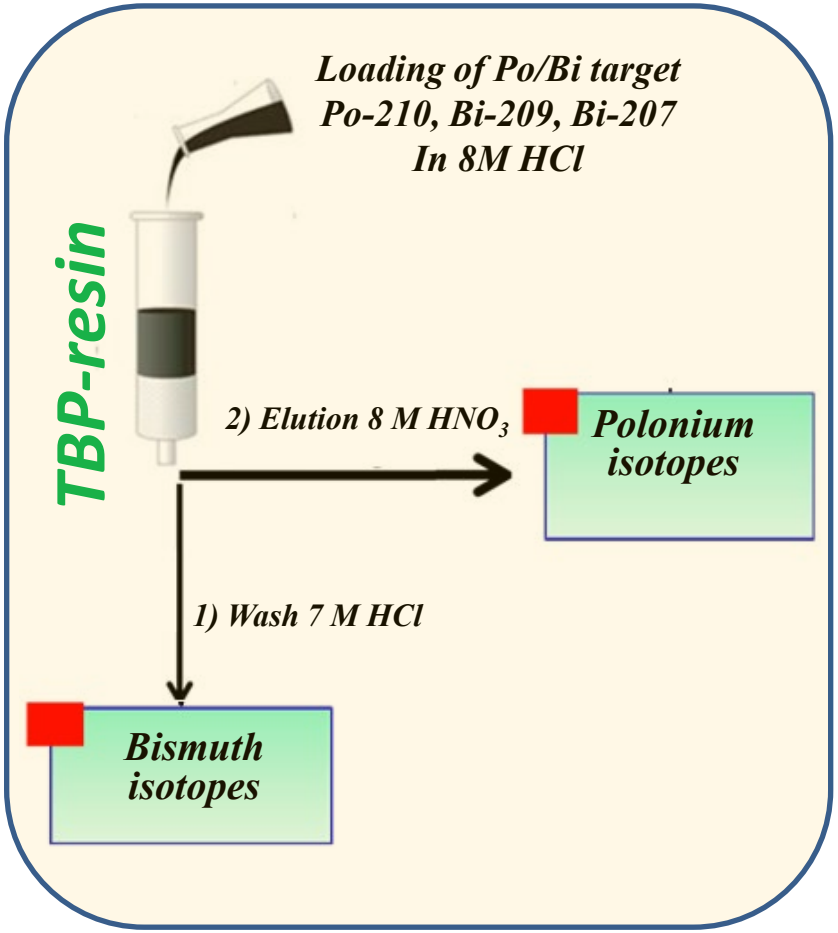
Po/ Bi Purification

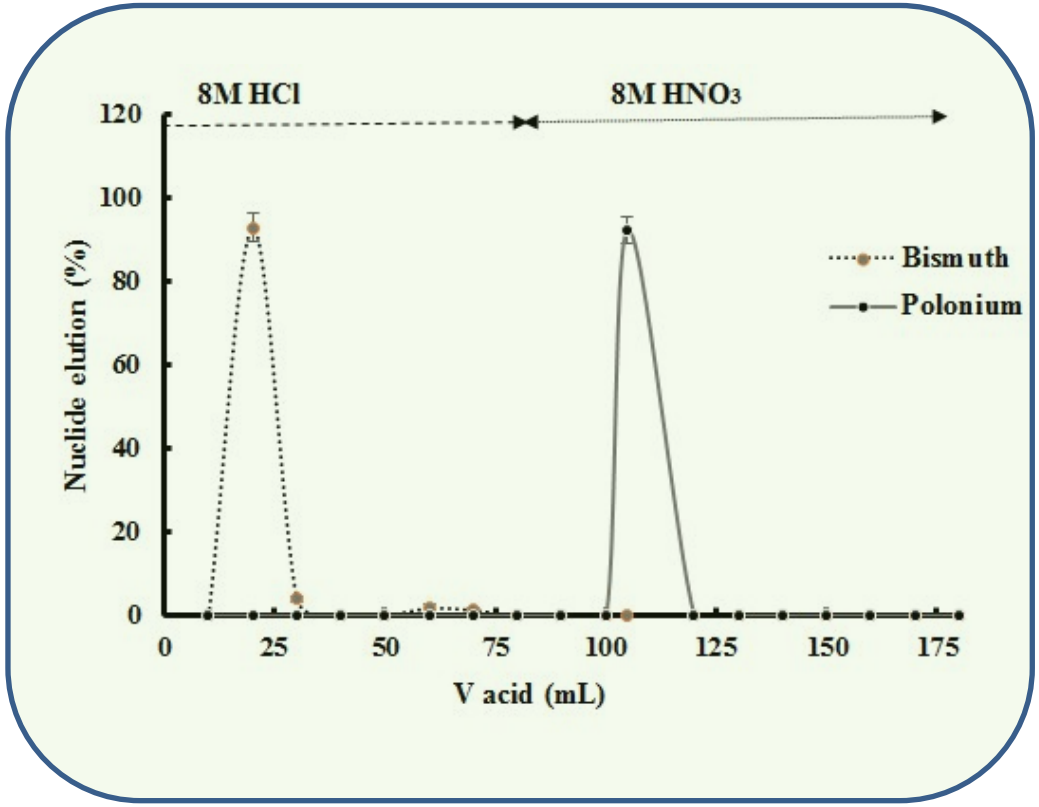


Comparison of Bi behavior over the functionalized TBP resin (represented as Kd,) over a range of different concentrations of HCl or HNO3 versus the liquid-liquid extraction with p-xylene (represented as the solvent extraction distribution coefficient D)

A. Younes et al. Journal of Radioanalytical and Nuclear Chemistry volume 324, pages 823–828 (2020)

Po/ Bi Purification

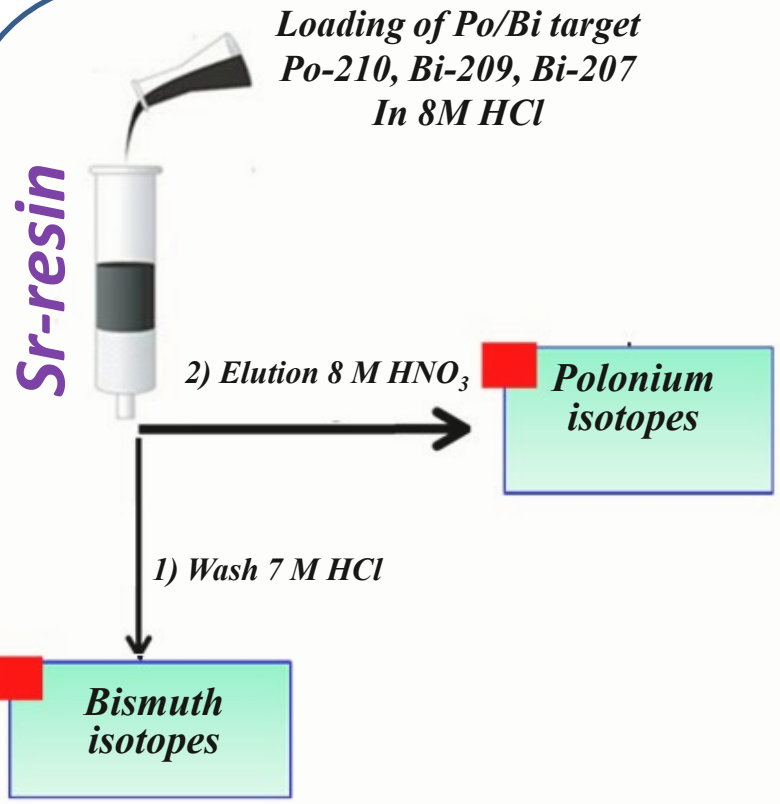


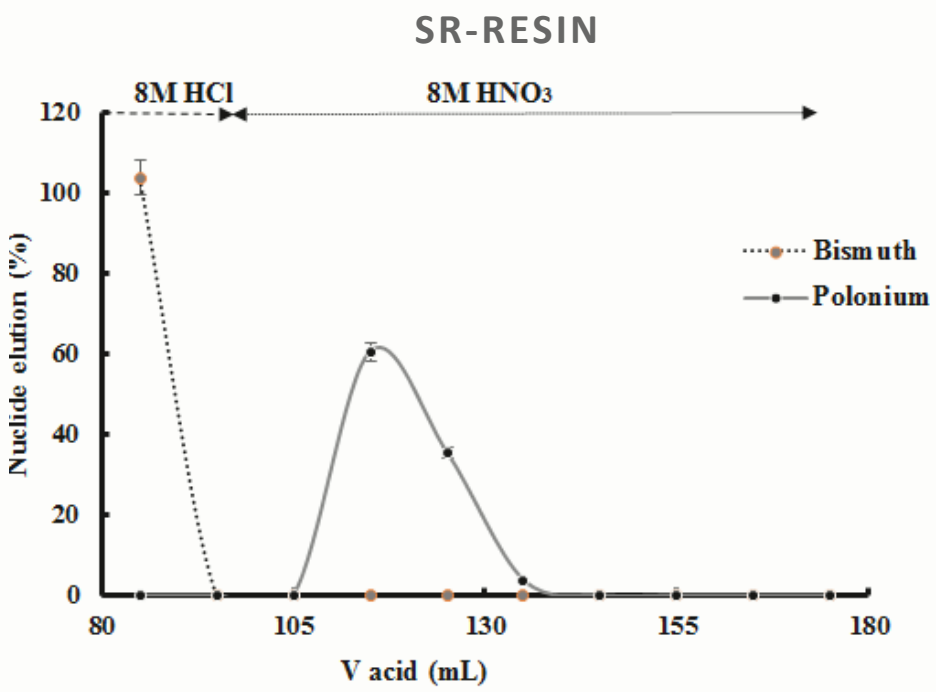


% Po recovery yield: 99 %

A. Younes et al. Journal of Radioanalytical and Nuclear Chemistry volume 324, pages 823–828 (2020)

Po/ Bi Purification



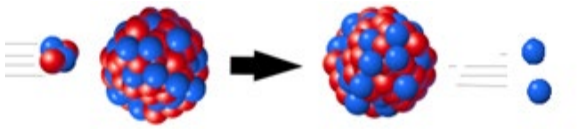


% Po recovery yield: 68 %

Conclusion

- **Production: Polonium can be produced using a cyclotron by ^{209}Bi (α,3n) ^{210}At reaction**

$$^{209}_{83}Bi + ^{4}_{2}He \longrightarrow ^{3}_{0}n + ^{210}_{85}At \longrightarrow ^{210}_{84}Po + ^{206}_{83}Bi$$



- **^{210}Po can be separated and purified from irradiated ^{209}Bi target :**
  - **liquid-liquid extraction using TBP in *para*-xylene /7M HCl followed by Back-extraction into 9M HNO_3. (% yield = 85 %)**
  - **TBP resin ion exchangers (% yield = 99%):**
    - **Bi eluted using 7M HCl**
    - **Po eluted in 8 M HNO_3**

Acknowledgments

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- Dr. Cyrille Alliot
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SUBATECH

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TRISKEM

- Dr. Steffen Happel
- Dr. Aude Bombard


THE GOOD NEWS: WE'VE FIGURED OUT WHY YOUR NOSE GLOWS.
UMM... THE BAD NEWS...
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12-3
POLAR PONTIFICATOR
POLONIUM-210 POISONINGS SPREAD
NEXT TIME SKIP THE CARROTS THAT THE KREMLIN LEAVES FOR YOU...