The Abdus Salam
International Centre for Theoretical Physics

United Nations
Educational, Scientific and
Cultural Organization

IAEA
International Atomic Energy Agency

**1833-5**

# Workshop on Understanding and Evaluating Radioanalytical Measurement Uncertainty

***5 - 16 November 2007***

## Current IAEA Activities for Development of Recommended Procedures of Radionuclides in Terrestrial Environmental Samples.

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# Current IAEA Activities for Development of Recommend Procedures of Radionuclides in Terrestrial Environmental Samples

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*IAEA - Agency's Laboratories, Seibersdorf*

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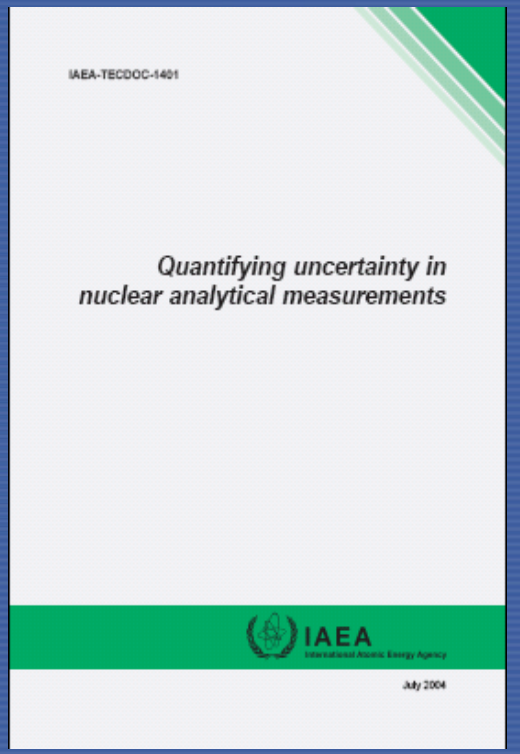
*Atoms for Peace: The First Half Century*
*1957–2007*

# Background

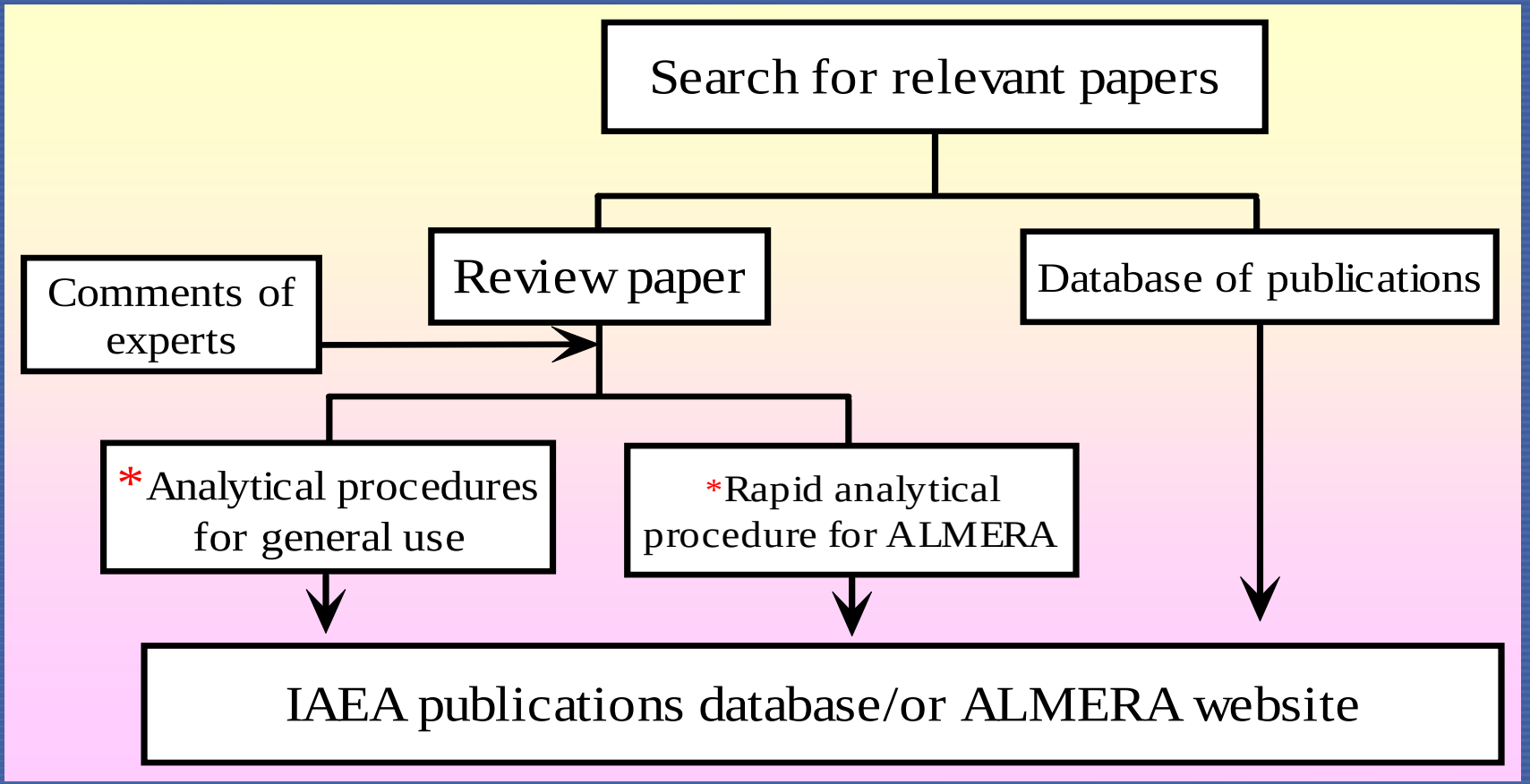
- Somewhat dated IAEA Technical Reports
  - ✓ No. 295 (IAEA, 1989).
  - ✓ Generic procedures for monitoring in a nuclear of radiological emergency (IAEA-TECDOC-1092, 1999)
  - ✓ Quantifying uncertainty in nuclear analytical measurement (IAEA-TECDOC 1401, 2004)
- Demands for the provision of analytical procedures of radionuclides from MS



# Objectives

- Since 2005, the IAEA's programme has included activities on the development of a set of procedures
- Upgrade IAEA technical report
- Provide MS with validated analytical procedures


# How to Approach ?




* : The procedures should not be regarded as “endorsed” by the IAEA for any particular purpose

# *Key points considered in development of procedures*

## Requirements on Analytical Procedures of Radionuclides

**Reliability**

- Accuracy
- Precision

**Analysis time**

- Rapid

**Cost**

- Cheap

# Activities in 2005 and 2006

- Review analytical method of Po-210 by alpha-spectrometry
- Review analytical method of Pu by ICP-MS
- automatic on-line sequential injection system for separation and preconcentration of radionuclides
- Sequential separation of Pb-210, Po-210, U, Th and Ra-226 in phosphogypsum.

# *Review paper of $^{210}$Po analysis in environmental samples*

- Review 130 papers
- 16 kinds of samples
- Separation techniques
  - Solvent ext.
  - Ion exchange
  - Extraction Chromatography
- Source preparation
- Alpha spectrum analysis
- Detection limit

| Sample | No. of paper |
|---|---|
| Air | 1 |
| Drinking water | 4 |
| Ground water | 3 |
| Freshwater | 6 |
| Rainwater | 4 |
| Seawater | 13 |
| Soil | 6 |
| Sediment | 9 |
| Coal | 1 |
| Tobacco | 8 |
| Phosphogymsum | 6 |
| Food | 9 |
| Lake fish | 1 |
| Human body | 12 |
| Plant | 5 |
| Biota | 13 |
| Analytical method | 29 |
| Total | 130 |

# *Review paper of Pu and its isotope ratio measurement in environmental samples*

- Review 164 papers
- Soil, sediment, water, biological, urine
- Adjustment of oxidation state
- Separation techniques
  - Anion exchange column
  - Liquid-liquid extraction
  - Solid phase extraction chromatography (e.g. TRU, TEVA)
  - HPLC
- Interferences by polyatomic ions, ($^{238}U^{1}H$ at m/z 239)
- Detection limit

CRITICAL REVIEW www.rsc.org/jaas | Journal of Analytical Atomic Spectrometry

**Determination of Pu isotope concentrations and isotope ratio by inductively coupled plasma mass spectrometry: a review of analytical methodology**

Cheol-Su Kim,*[a] Chang-Kyu Kim,[b] Paul Martin[b] and Umberto Sansone[b]

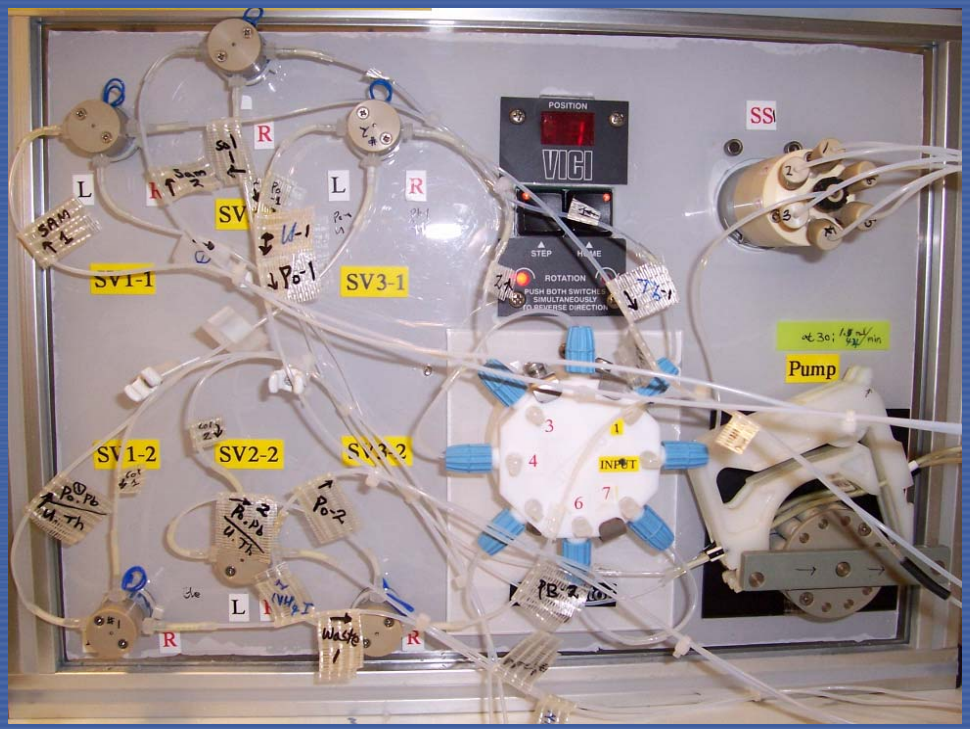
*Received 1st December 2006, Accepted 14th March 2007*
*First published as an Advance Article on the web 29th March 2007*
DOI: 10.1039/b617568f

# *Automatic on-line sequential injection (SI) system*

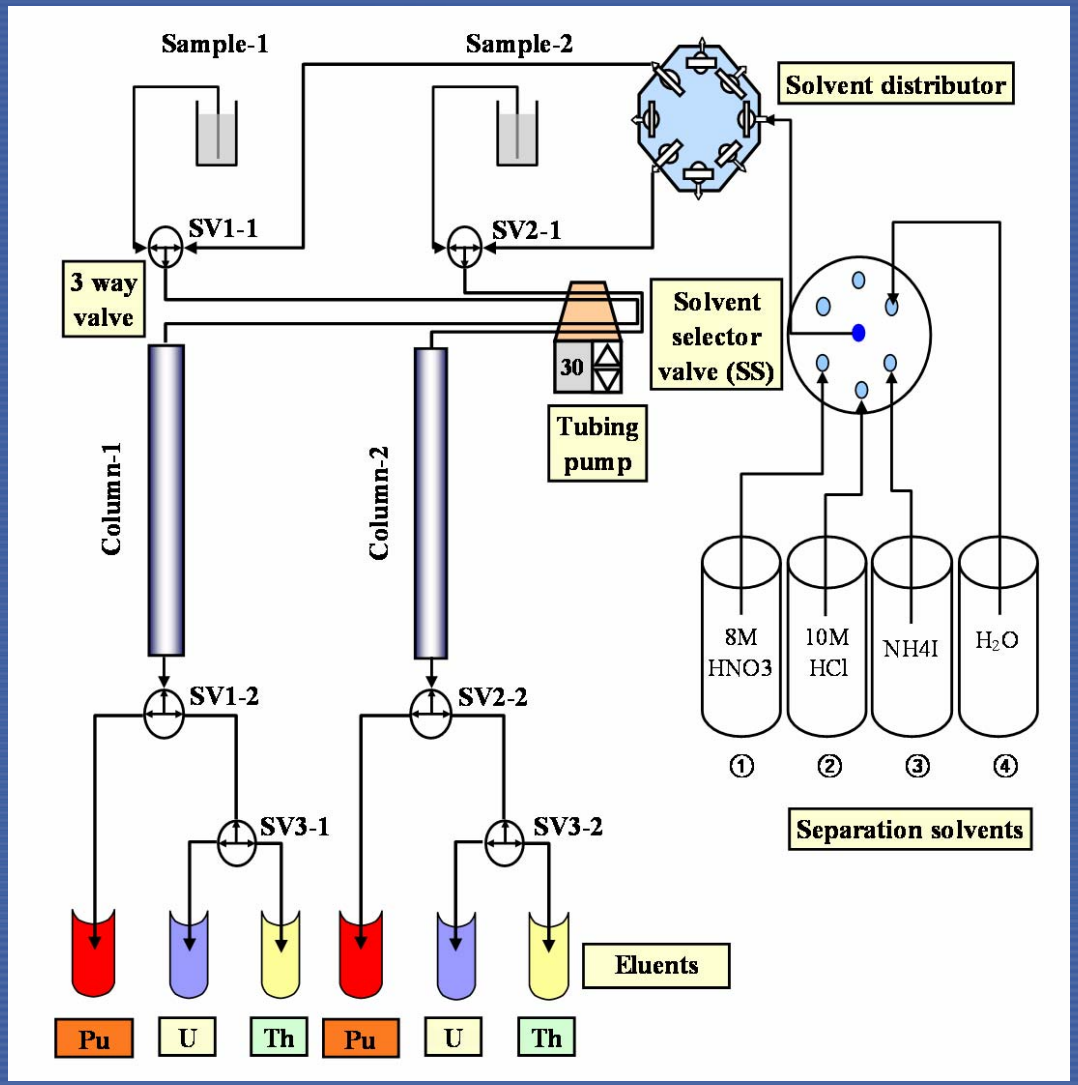
- **to shorten separation time of radionuclides in chromatography**
- **keep the flow rate of solution constantly**
- **avoid clogging or bubbling in a chromatographic column**

## The SI system

- 6-ports solvent selection valve
- solvent distributor
- six 3-way isolation valves
- two channel peristaltic pump
- two chromatographic columns
- Extendable to max. 8 columns



# *A schematic diagram of the on-line SI system for separation of Pu*

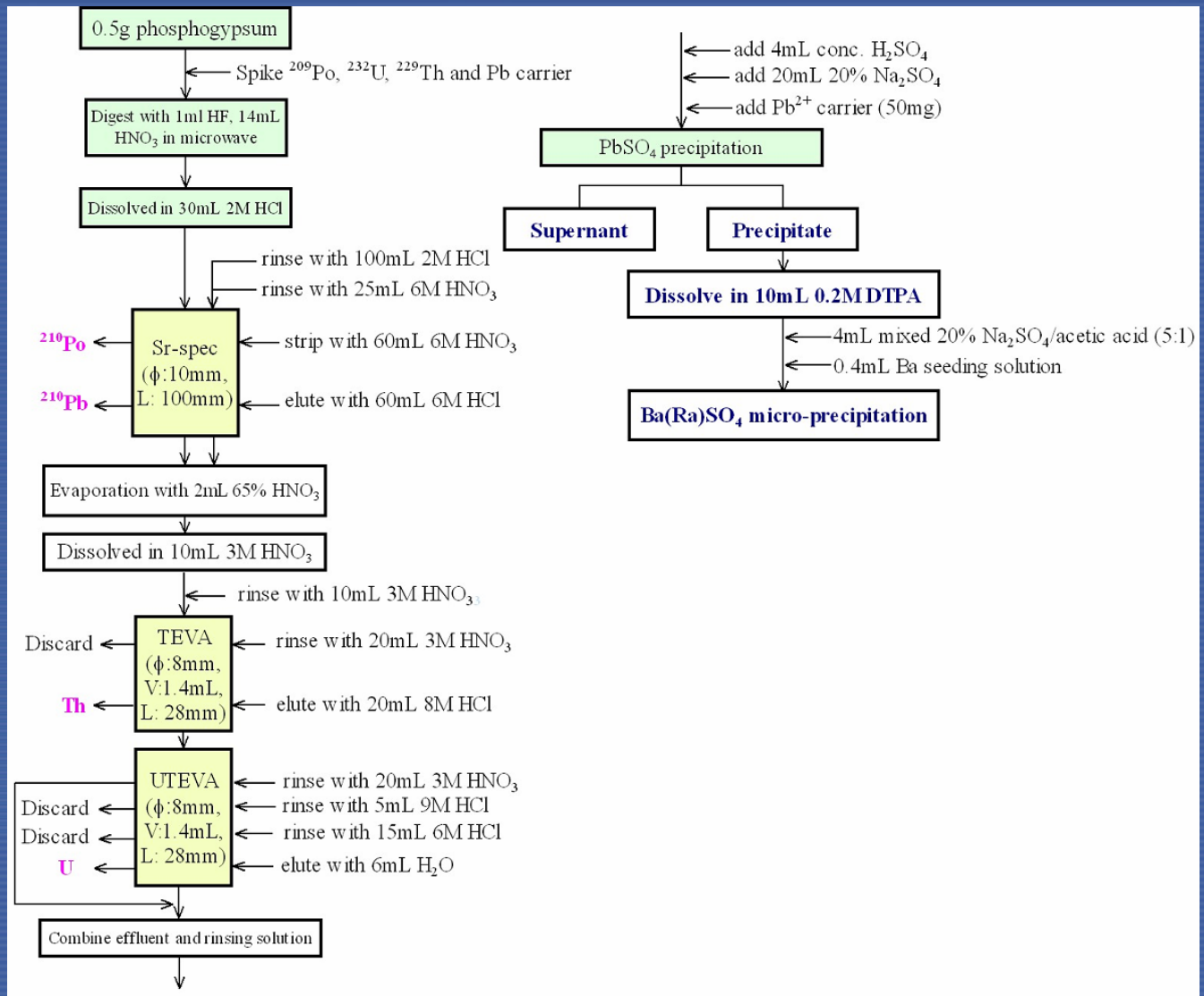


## *Determination results of $^{239+240}$Pu in IAEA reference material (Soil-6) by the on-line SI system*

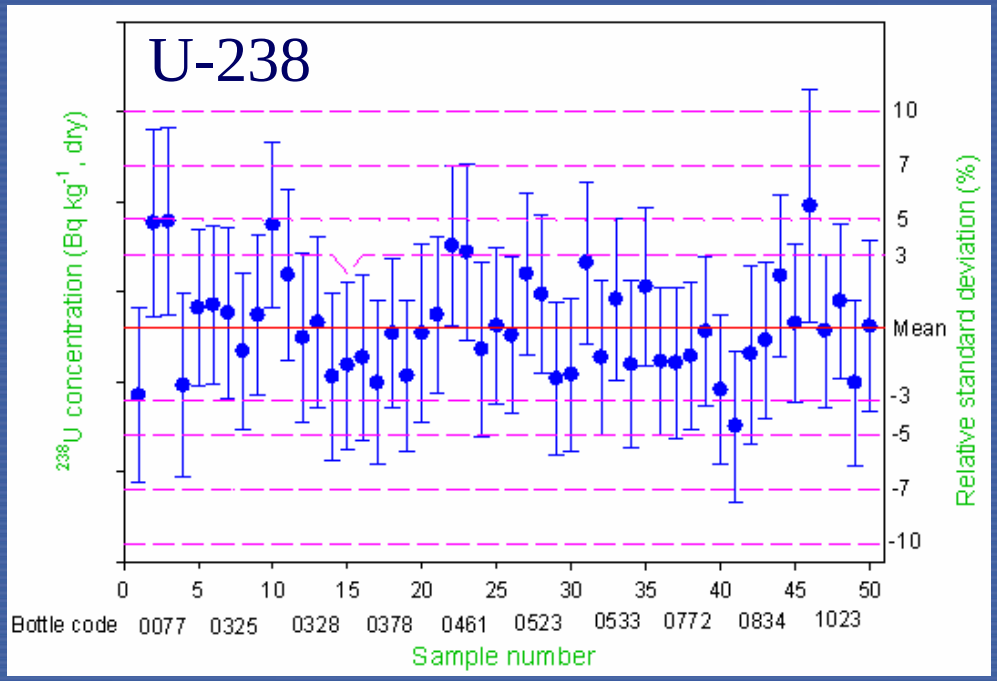
| No. of replicates | Activity concentration (Bq kg$^{-1}$, dry) | z-score | Chemical recovery (%) |
|---|---|---|---|
| 1 | 0.96 ± 0.05* | -1.94 | 92 |
| 2 | 1.06 ± 0.05 | 0.49 | 91 |
| 3 | 1.03 ± 0.05 | -0.24 | 96 |
| 4 | 1.01 ± 0.05 | -0.73 | 82 |
| 5 | 1.07 ± 0.05 | 0.73 | 85 |
| 6 | 1.01 ± 0.13 | -0.73 | 72 |
| 7 | 1.04 ± 0.15 | 0.00 | 95 |
| 8 | 1.10 ± 0.14 | 1.46 | 82 |
| 9 | 1.06 ± 0.13 | 0.49 | 90 |
| **Average** | **1.04±0.04**** | | **87±8** |

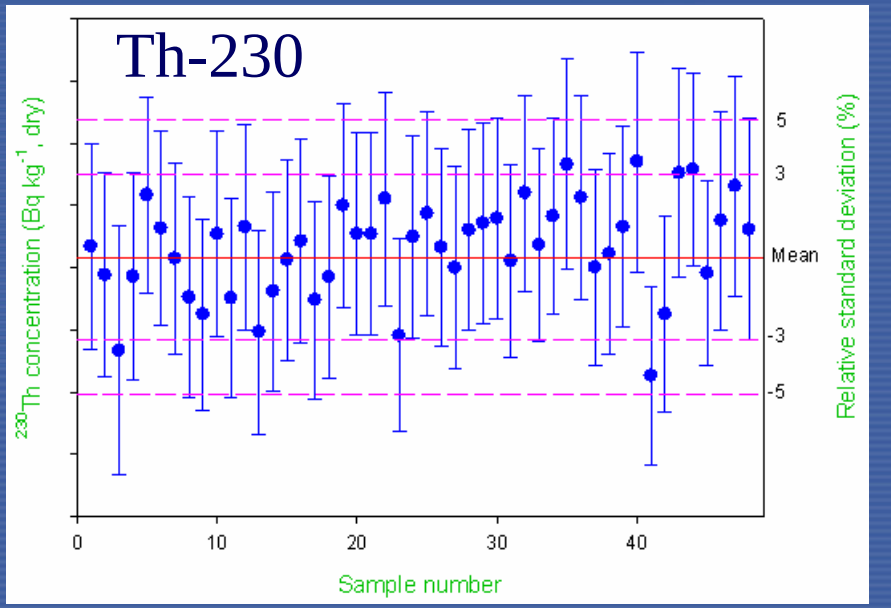
* = combined uncertainty
** = standard deviation (1σ)

# Sequential separation method for homogeneity test of natural radionuclides in phosphogypsum



# Homogeneity test results of U and Th in phosphogypsum

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# What we are doing in 2007 !

- Method validation of two candidates method of $^{210}$Po in water samples and prepare a recommended procedure
- Rapid method of Pu in soil sample by alpha-spectrometry
- Prepare a paper on combined uncertainty evaluation in the calculation of $^{210}$Pb and $^{210}$Po activities on sampling date

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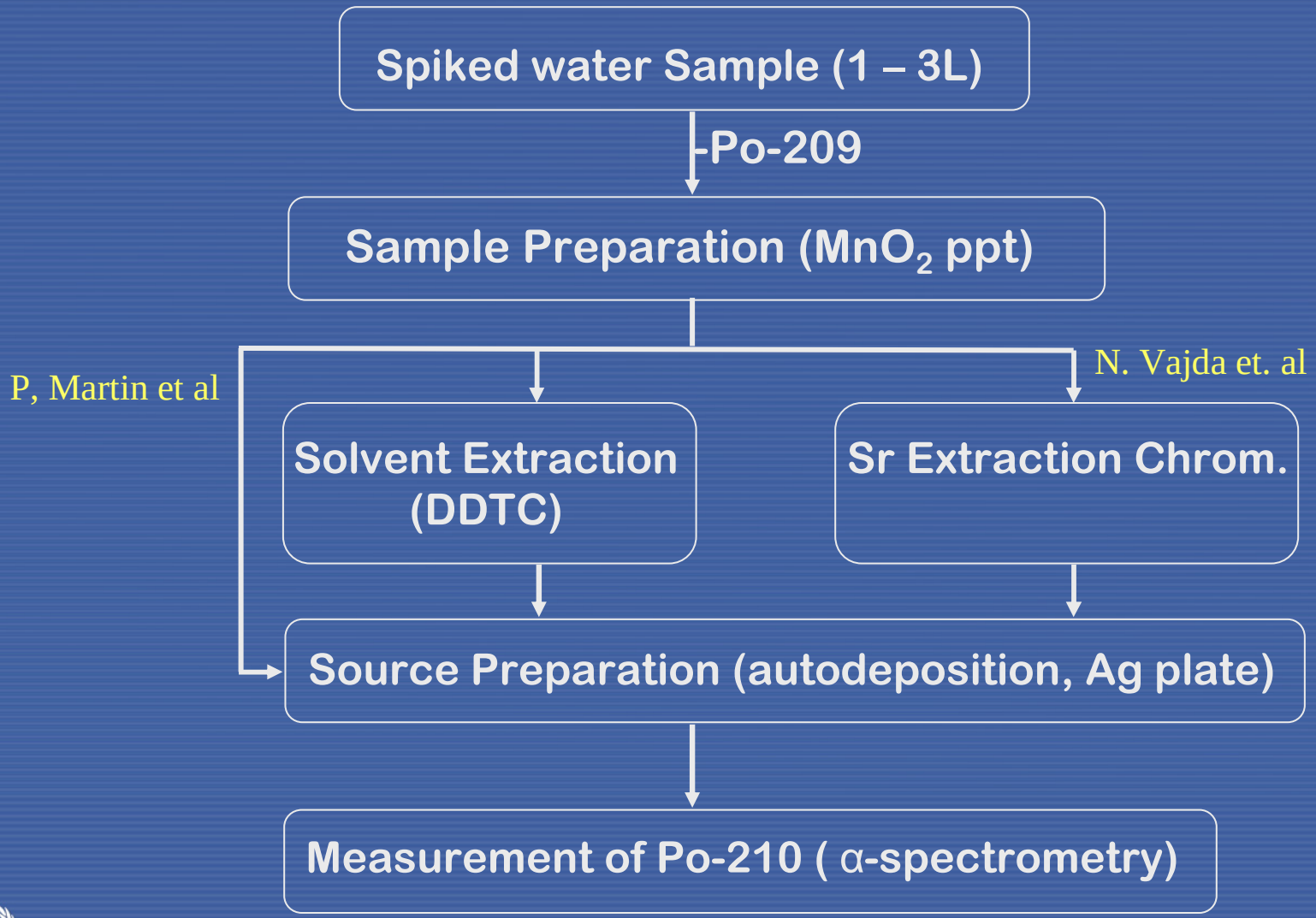
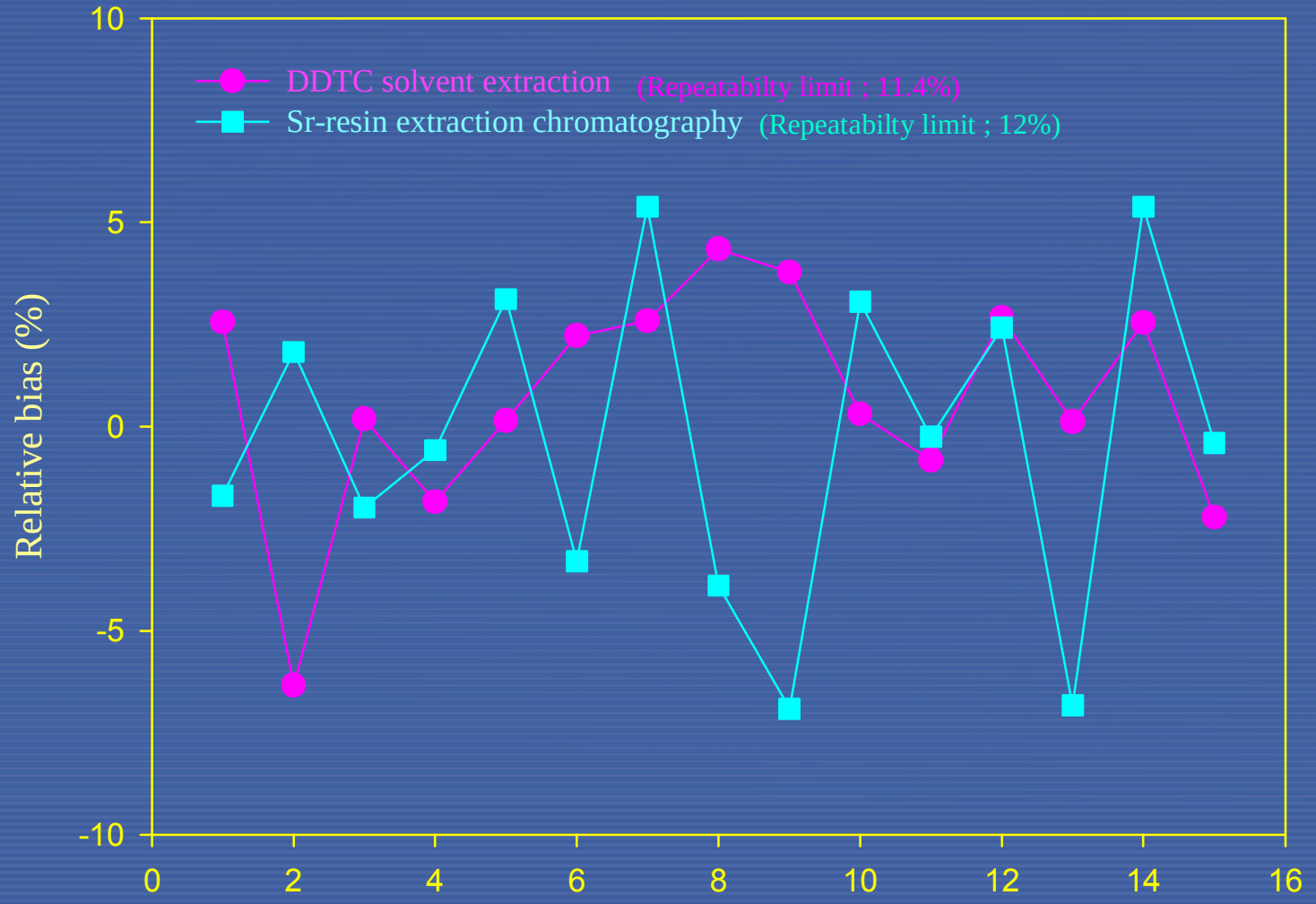
# Outline of Radiochemical Separation of $^{210}Po$ in water sample



# Relative bias and Repeatability (in 10mBq/l of $^{210}Po$)

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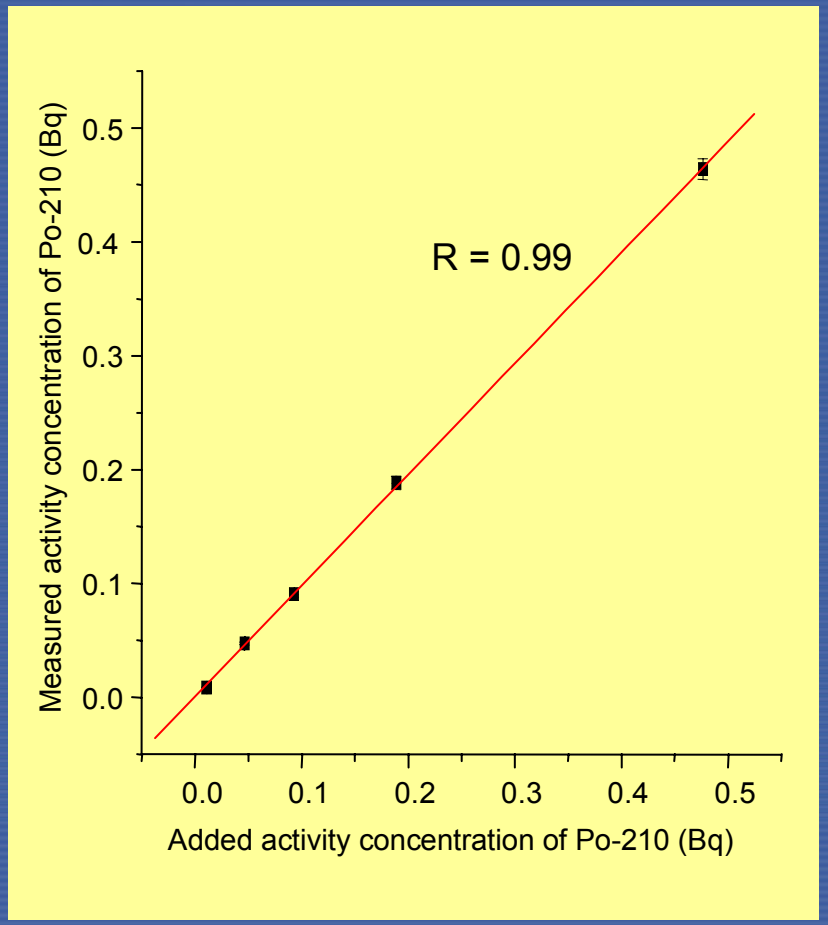
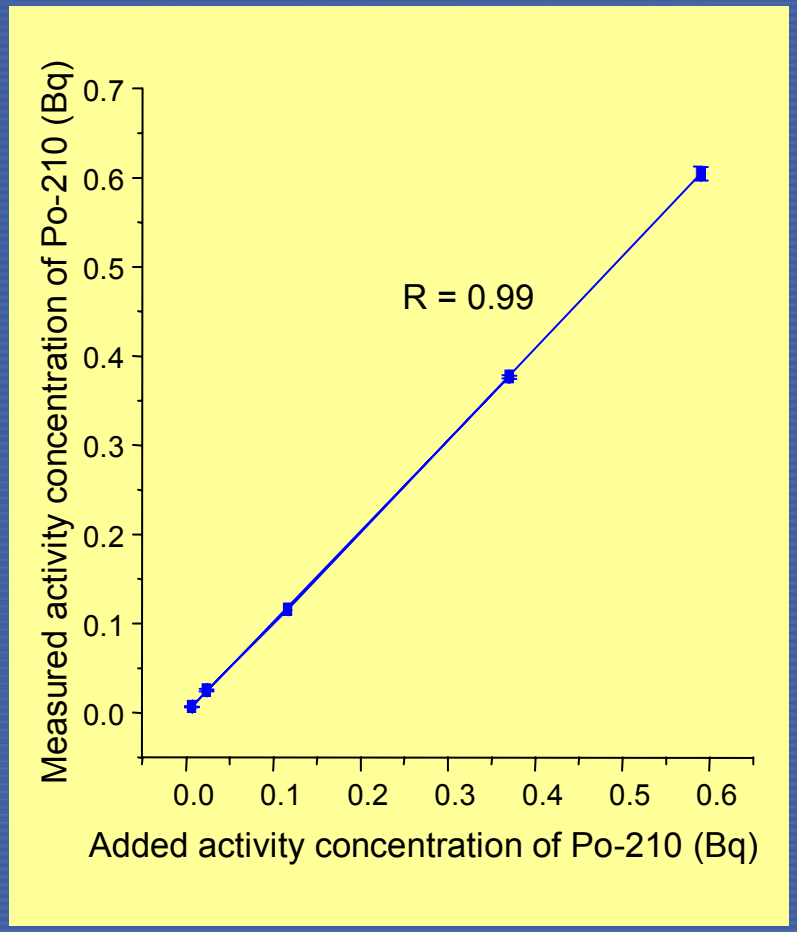
# Linearity

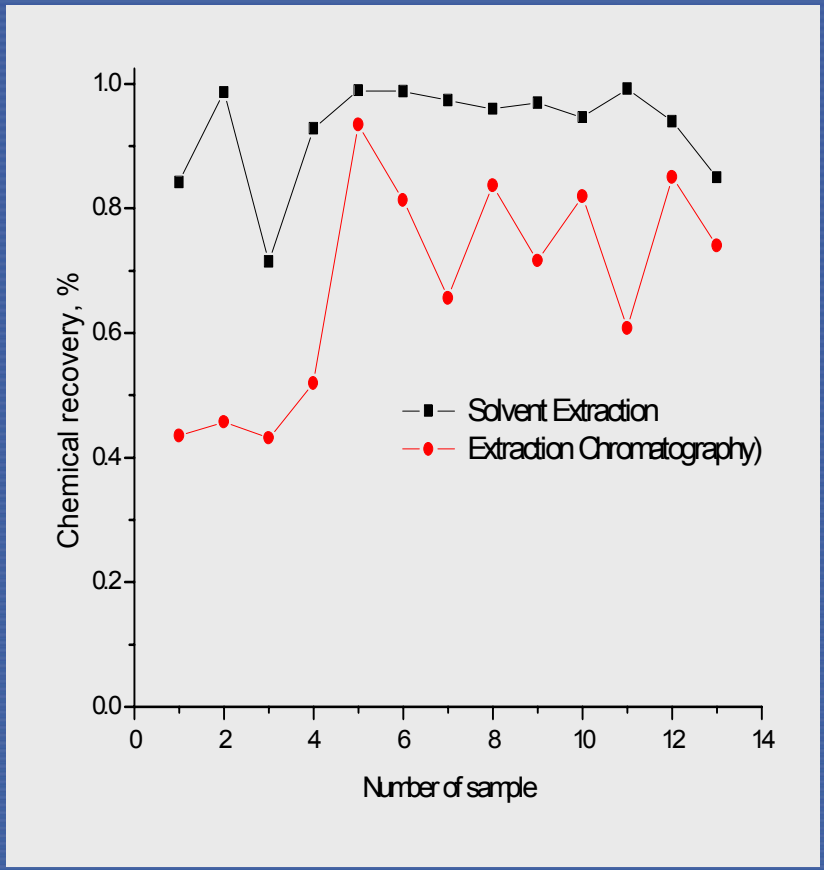
## (a) Solvent extraction




## (b) Extraction chromatography



# Chemical recovery




| No. of reused of Sr resin | 1st | 2nd | 3rd | 4th | 5th |
|---|---|---|---|---|---|
| Chemical yield (%) | 55 - 82 | 60 - 84 | 43 - 85 | 20 - 50 | 3 - 20 |

# Analysis Time (1 set / 4 samples)

**Sample Preparation (6 hours)**
- -Weighing of samples and adding tracers : 1 hr
- -Stirring the sample solution after adding tracers : 1 hr
- -Preparation of $MnO_2$ ppt : 1 hr
- -Stand $MnO_2$ ppt : 2 hrs
- -Centrifuge $MnO_2$ ppt and dissolving it with 5 M or 2 M HCl (1% $H_2O_2$): 1 hr

**Solvent Extraction (total : 7 hrs)**
- -Preparing solvent solution : 1 hr
- -Solvent extraction : 1.5 hr
- -Evaporation of solution : 2.5 hrs
- -Source preparation : 2 hr

(Total analysis time : 13 hrs)

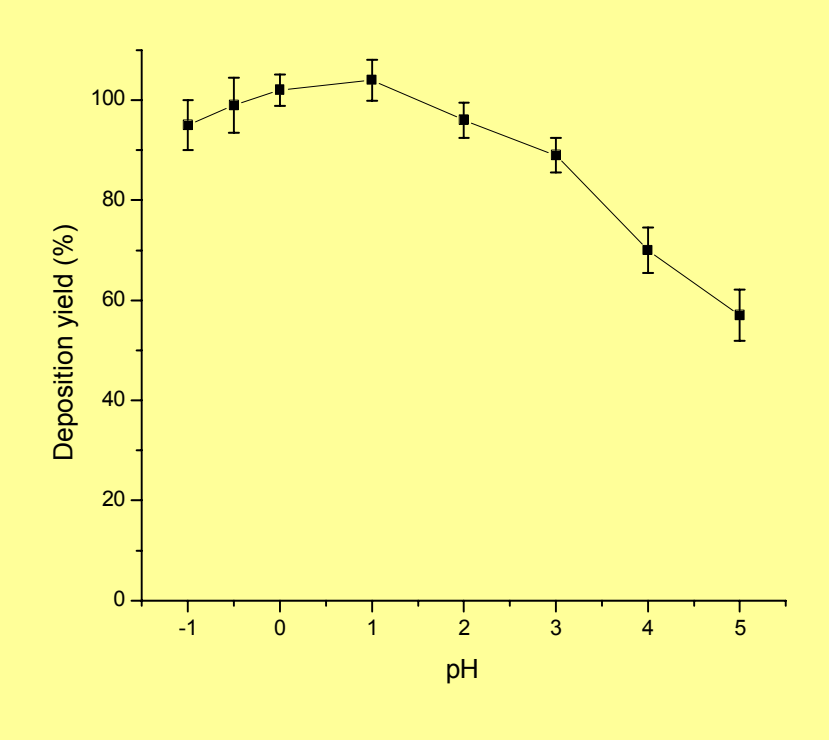
**Extraction Chromatography (total : 15 hrs)**
- -Preparation of column : 1 hr
- -Precondition of column : 1 hr
- -Sample loading and elution : 3 hrs
- -Regeneration of column : 2. 0 hrs
- -Evaporation of solution : 6 hrs
- -Source preparation : 2 hr

(Total analysis time : 21 hrs)

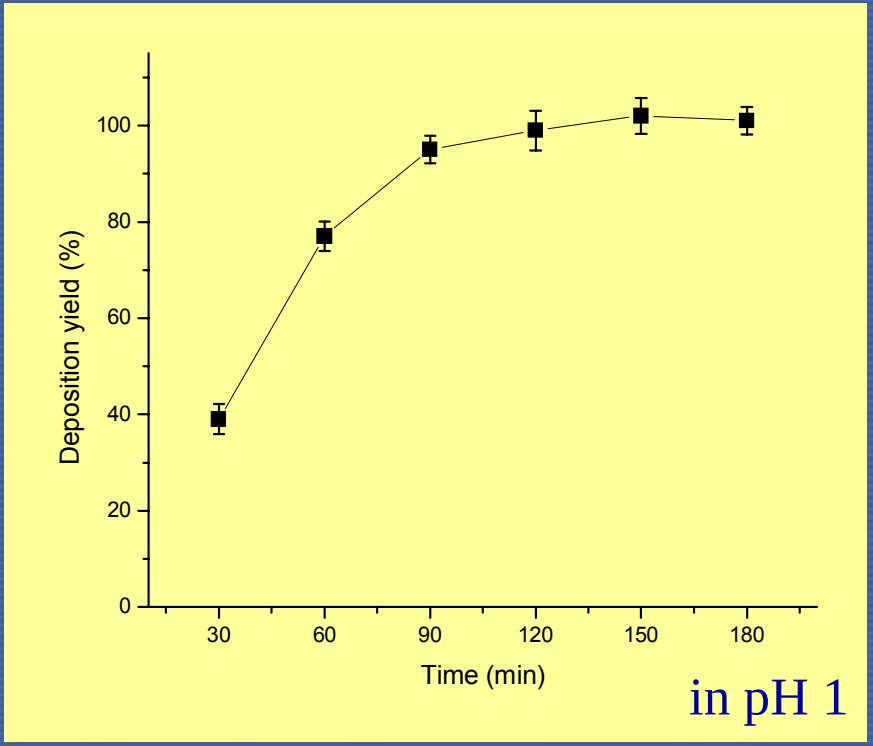
# Comparison results of two methods

| Items | Solvent Extraction | Extraction Chromatography |
|---|---|---|
| Linearity | R = 0.99 | R = 0.99 |
| Repeatability limit (in 3mBq/L) | 11 % | 12% |
| Analytical time | 13 hrs | 21 hrs |
| Analytical cost (for only chemical reagent) | 5 € (4 samples) | 70 € (4 samples, 5 times used) |
| Peak resolution | ~ 20keV | ~ 20keV |
| Chemical recovery | > 90 | > 80 |

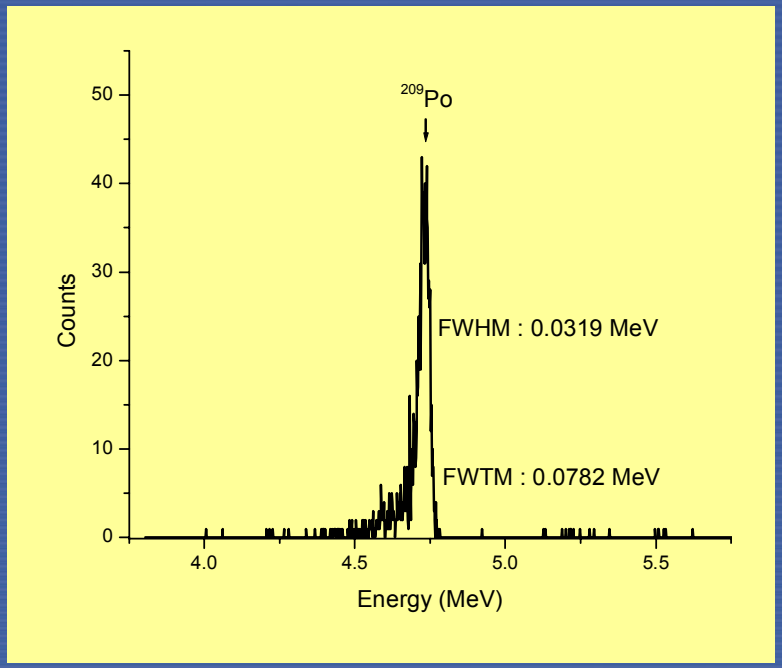
# Optimization of source preparation



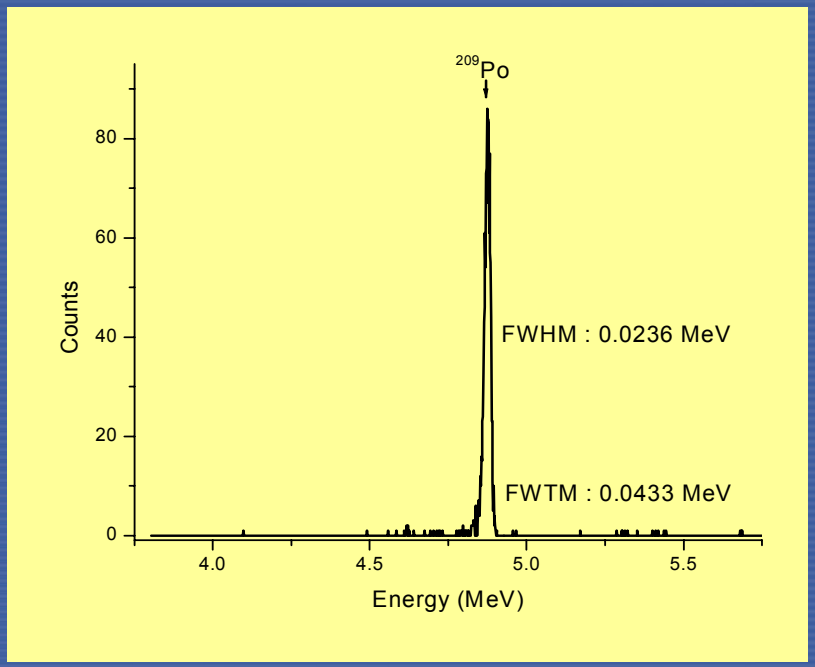

Variation of the deposition yield of $^{209}$Po with pH




Variation of the deposition yield of $^{209}$Po with the deposition time

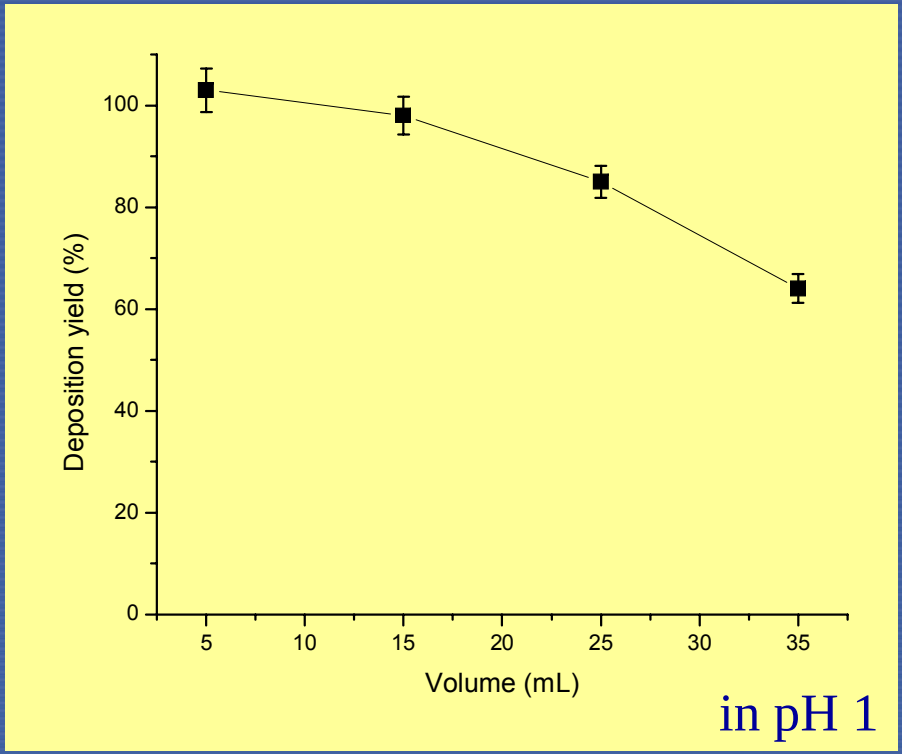



(a) pH : -1.0

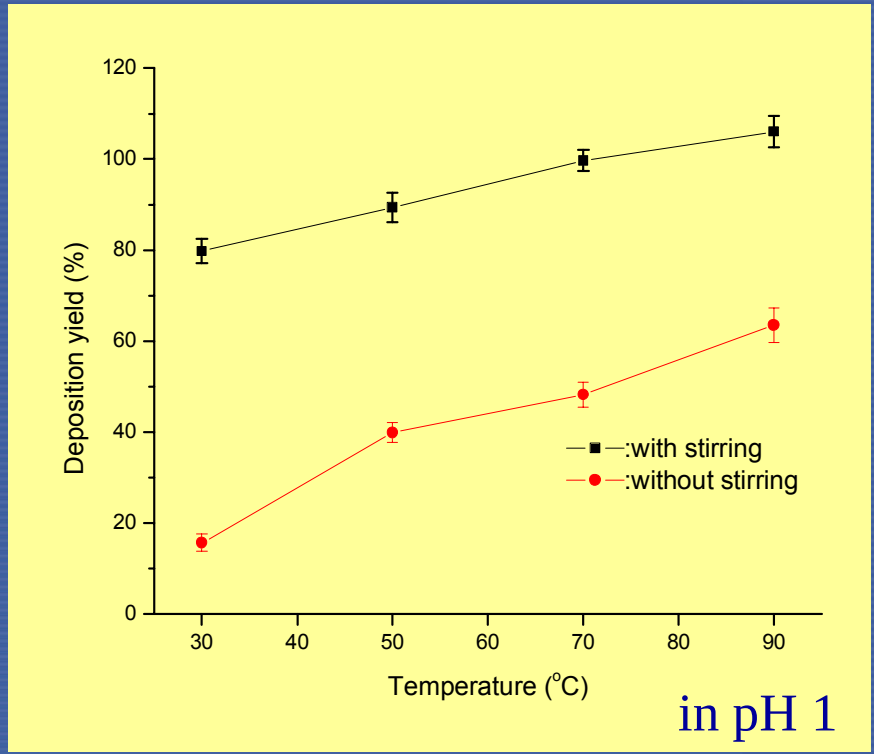



(b) pH : 0.0

Spectral resolution of $^{209}$Po at different pHs




Variation of the deposition yield of $^{209}$Po with the deposition solution volume




Variation of the deposition yield of $^{209}$Po with the temperature

# Optimum conditions for auto deposition of Po

| | |
|---|---|
| pH of deposition solution | 1.0 |
| Deposition time | 1.5 h |
| Deposition volume | 10 mL |
| Temperature | 90 $^{O}$C with stirring |

# *Rapid method of Pu in soil by α spectrometry*

- Background
  - *ICP-MS ; expensive, considerable skill operation*
  - *α spectrometry* ; most commonly used
  - ALMERA network ; require rapid results in emergency case
  - Conventional method ; time-consuming

# *How to approach*

- Literature review
- Experiments

  testing of fusion

  testing of coprecipitation

  testing of extraction chromatography:

    UTEVA

    TRU
- Selection of candidate method

# *Criteria for rapid method of Pu*

- For emergency
  - ✓small sample: 0.1 – 1 g, even including HP
  - ✓simple & effective procedure
  - ✓α spectrometry
  - ✓rapid:  within 1 day
- Generally applicable for
  - ✓Soil, sediment…environment
- Extension for other actinides

# *Separation of Pu according to the literature*

- Anion exchange chromatography
- Liquid-liquid extraction:
  HDEHP…
- Extraction chromatography

# *Extraction chromatography for Pu analysis in the literature*

- TEVA
- TRU for ICP MS
- UTEVA for ICP MS
- UTEVA – TRU
- Other combinations
  e.g. TEVA – UTEVA- TRU (Horwitz)

Single column procedure is preferred!

# *Standard procedures*

- ASTM, ISO, IAEA
  **anion exchanger**

- ISO/DIS 18589-4: DRAFT - 2007
  - ✓ Measurement of Pu isotopes by alpha spectrometry:
  - ✓ 0.1 – 100 g soil
  - ✓ acid digestion
  - ✓ Ca oxalate coprecipitation
  - ✓ separation:
    - liquid-liquid extraction by **HDEHP** or
    - ion exchange by **anion column** or
    - extraction chromatography: **TRU in 3M HNO3/Al/asc. acid**
  - ✓ electrodeposition or micro-coprecipitation

- ASTM C1310-95:
  Flow injection for actinide analysis by MS: **TRU**

# *Traditional Pu separation procedure*

- Acid destruction/leaching
- Anion exchange from
  8M $HNO_3$/$NaNO_2$
  Th removal with 9M HCl
  Pu(III) strip with 9M HCl/NH4I
- Evaporation
- Alpha source preparation

Selective for Pu
Robust

Big columns:
Time-consuming
Acid consuming
No need for preconcentration
(except for big samples)

Not extendable
for other actinides

# *Concept of the `rapid` procedure*

- Complete sample destruction – **fusion**
- **Preconcentration** in acidic media
- Separation by **extraction chromatography**

  Use of small **single** extraction chromatographic column
- Alpha source preparation either by electrodeposition or micro-coprecipitation

Selective for Pu
Robust

Small columns:
Rapid
Acid saving
Need for preconcentration

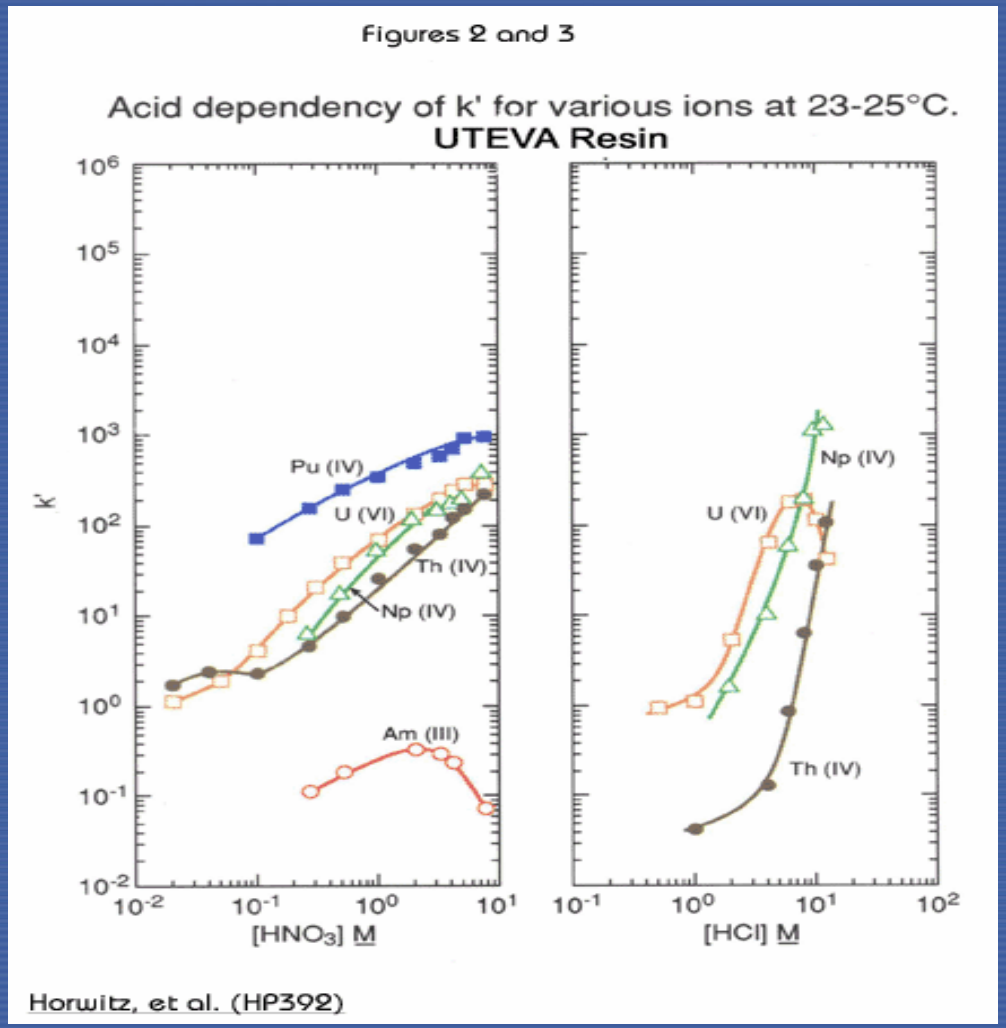
Extension
for other actinides:
Am (Np, U, Th)

# *Extraction chromatographic materials – commercially available*

E.P. Horwitz, Eichrom Co.

- TEVA
- UTEVA
- TRU
- DGA
- DIPEX
- DIPHONIX

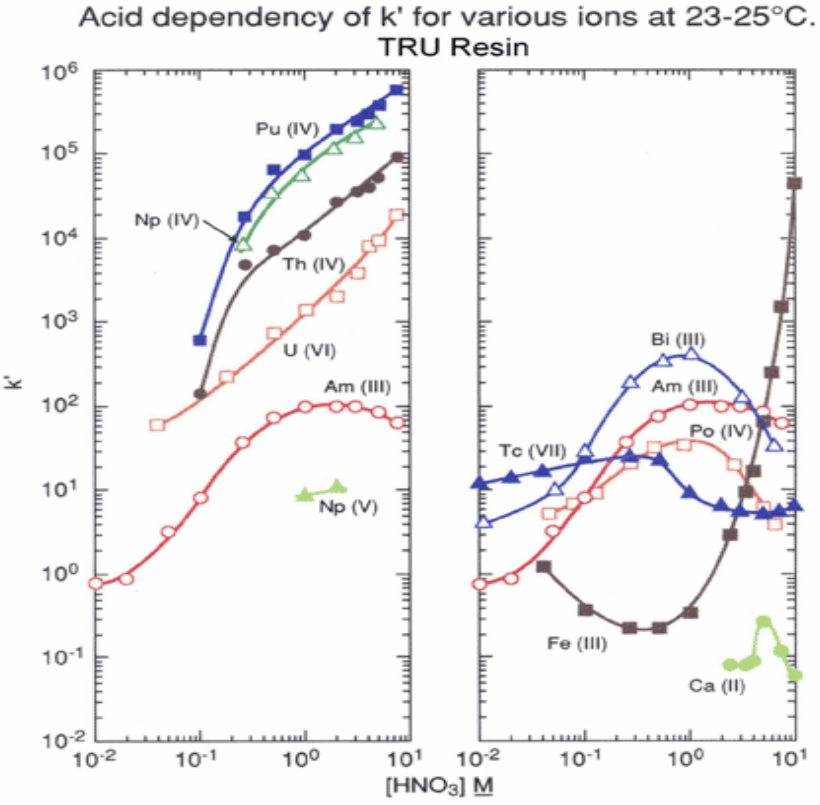
# UTEVA




- UTEVA is known as
- U selective sorbent,
- sorbent for IV and VI valence actinides

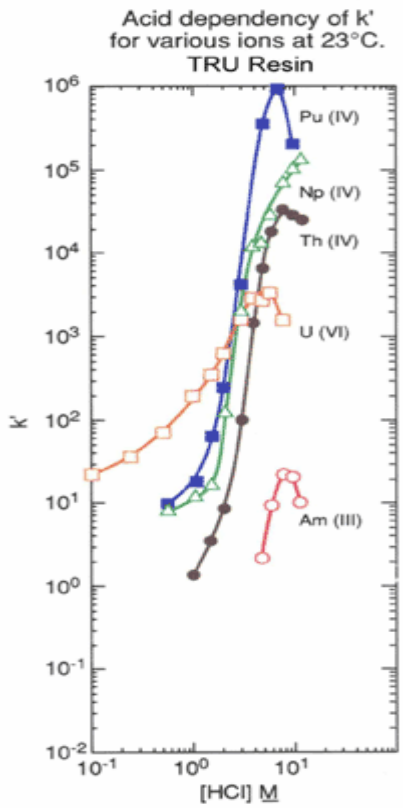
# TRU

Figure 2




Horwitz, et al. (HP193)

Figure 3




Horwitz, et al. (HP193)

- TRU is known as sorbent for III, IV, VI valence actinides

# UTEVA and TRU

- **Lack of knowledge:**
  - **different oxidation states**
  - **effect of matrix components**

# *Experiments*

- Fusion
- Coprecipitation
- Extraction chromatography: UTEVA
- Extraction chromatography: TRU
- Sequential separation of other actinides

# *Fusion of soil and sediment*

0.5 g IAEA-soil-6, IAEA-SL-3, NBS-4355, NIST-694

Std: $CaO$, $SiO_2$, $Al_2O_3$

Fusion tests in the Fluxer, in Pt dishes:

| | |
|---|---|
| **$LiBO_2$** | some un-attacked $SiO_2$ |
| KF | not good for refractory oxides |
| pyrosulfate | not good for silicates |
| KF-sulfuric acid –pyrosulfate | foaming, spraying |
| KF – $LiBO_2$ | insoluble salts |
| **KF – acid volatilization – $LiBO_2$** | foaming, spraying |

**Dissolution in 100 mL 1M HCl.**

# *Coprecipitation of actinides with $CaF_2$*

**From 100 ml 1M HCl containing the $LiBO_2$ fusion cake**

**+ 50 mg Ca**

**+ 20-30 mL 40% HF**

**Filtration through small membrane.**

ACIDIC

| | Oxidation state adjustment | Pu yield % | U yield % |
|---|---|---|---|
| CP1 | - | 98 | |
| CP2 | - | | 38 |
| CP4 | Fe(II) $N_2H_4$ | | 99 |
| CP5 | Fe(II) $N_2H_4$ | 105 | |

# *Coprecipitation of actinides with Ca oxalate*

**From 100 ml 1M HCl containing the $LiBO_2$ fusion cake**

**+ 50 mg Ca**

**+ 3 g oxalic acid**

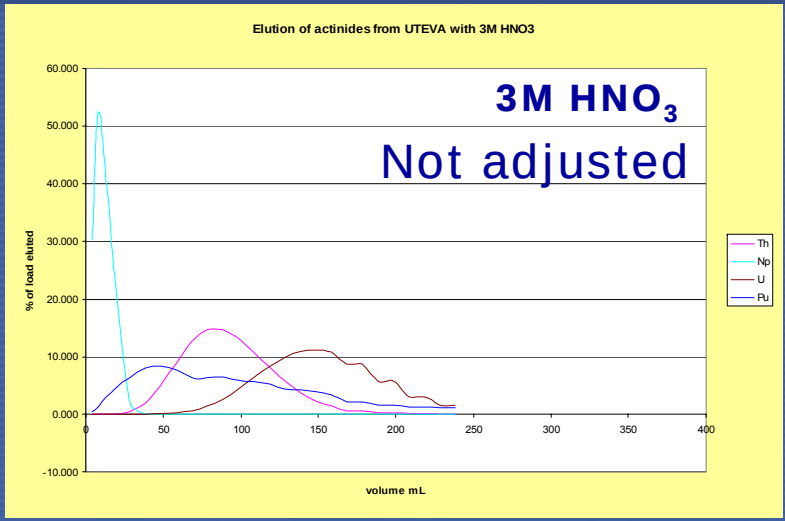
**+ $NH_3$ to pH 1-3**

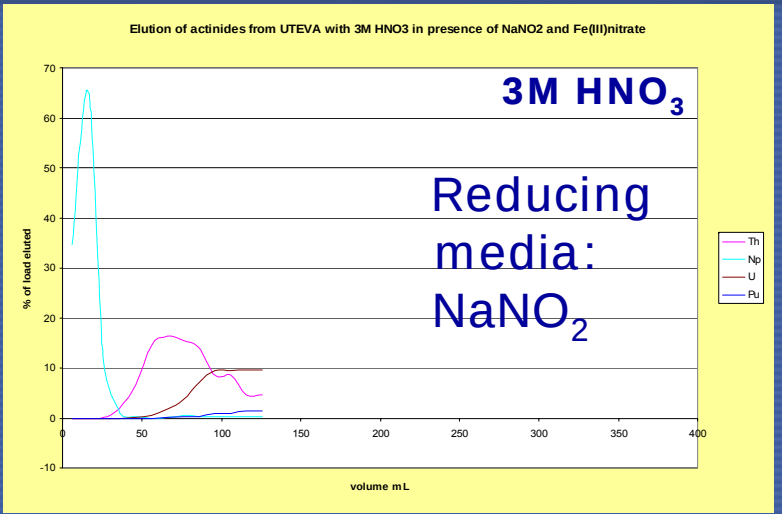
**Filtration through small membrane.**

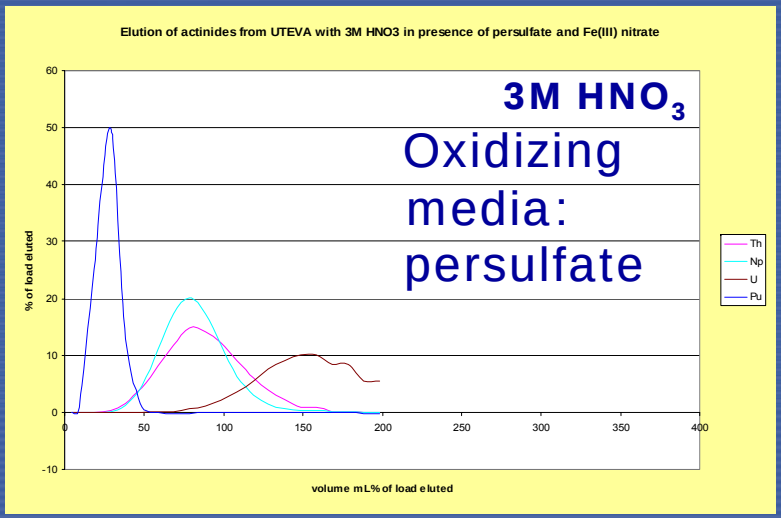
LESS ACIDIC

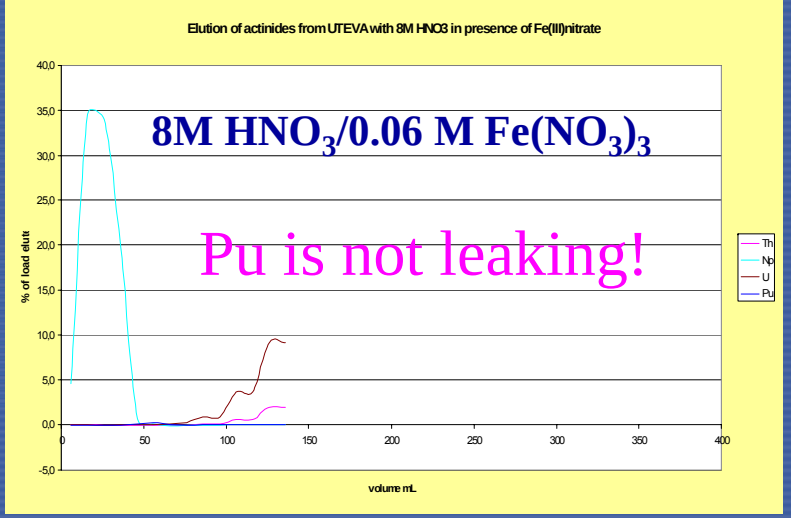
| | Oxidation state adjustment | Pu yield % | U yield % |
|---|---|---|---|
| CP8 | - | | 8 |
| CP11 | - | 6 | |
| CP6 | Fe(II)<br>$N_2H_4$ | 96 | |
| CP7 | Fe(II)<br>$N_2H_4$ | | 88 |

# UTEVA Resin: elution of actinides



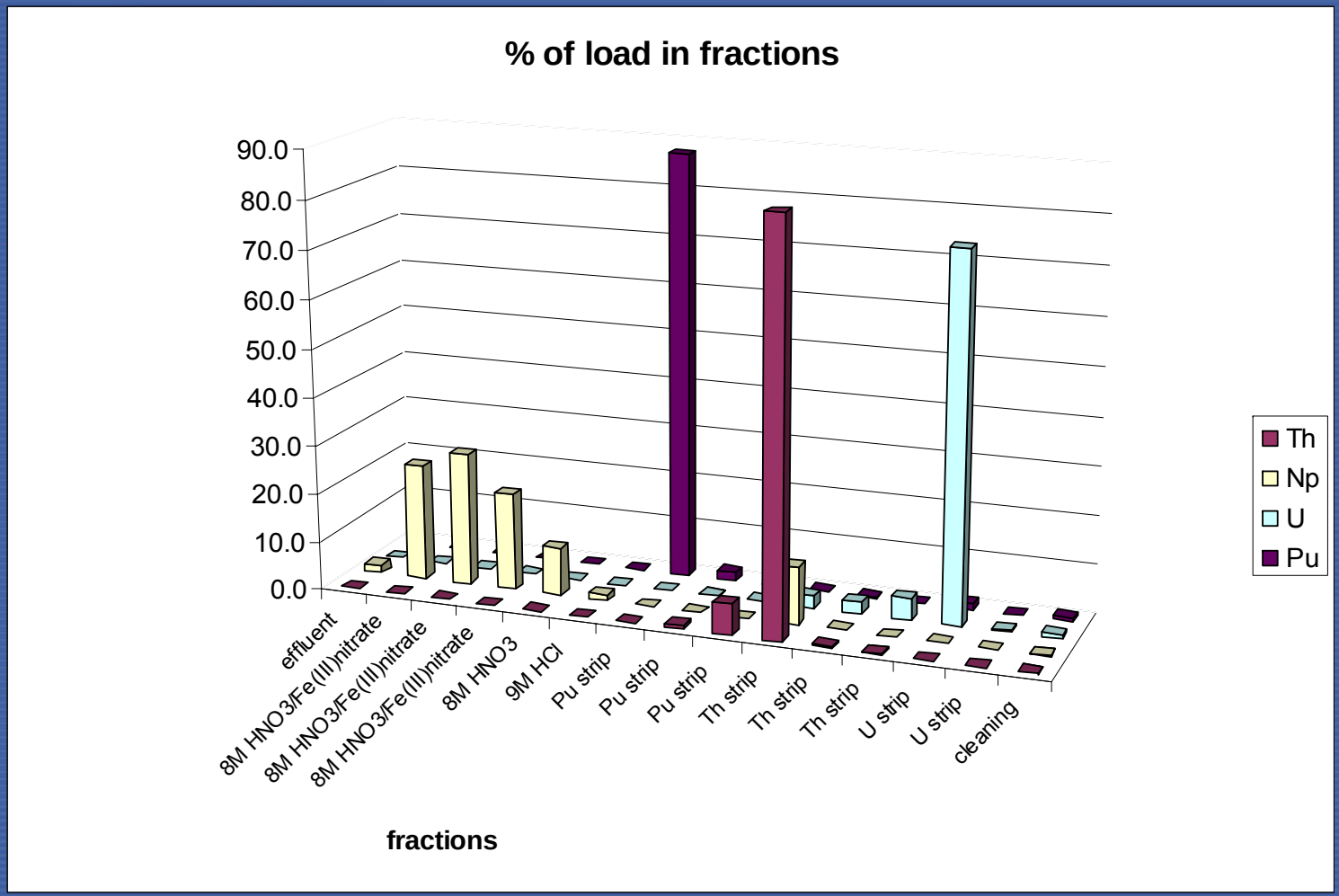



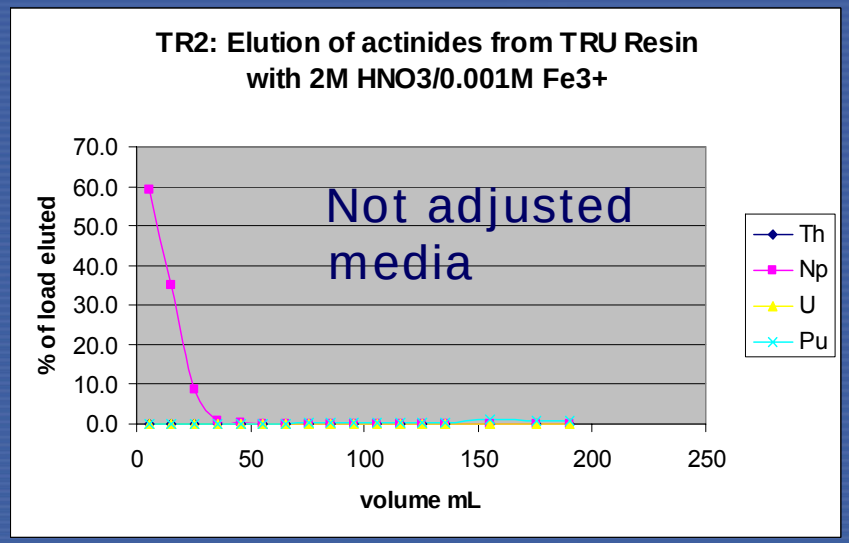



Load: 8M $HNO_3$/Fe(III)
Pu strip: 9M HCl/0.1M NH4I
Th strip: 4M HCl
U strip: 0.1M HCl
Am is lost

UTEVA (34mm)



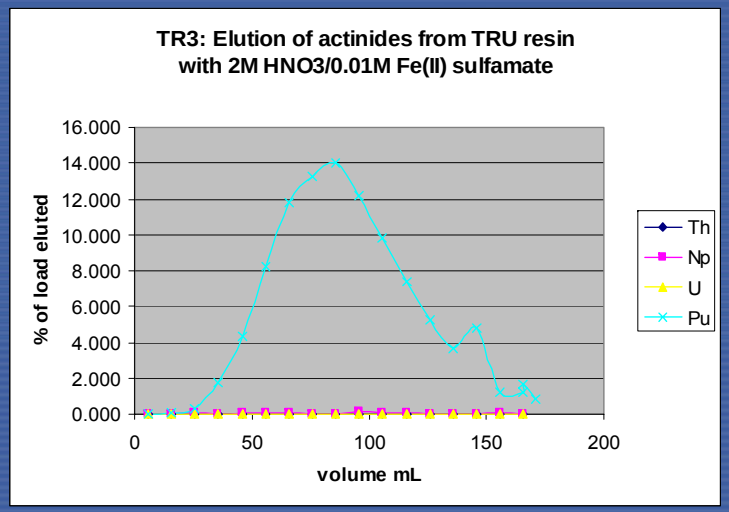
# TRU resin: elution of actinides

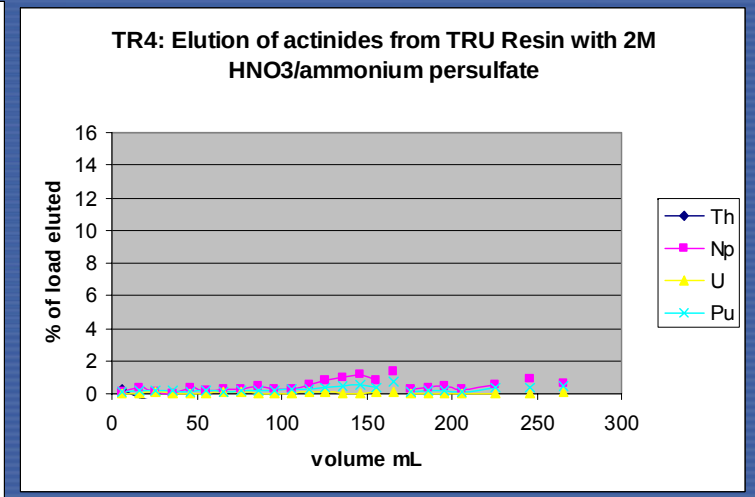



2M $HNO_3$

Oxidizing media: persulfate

Reducing media: Fe2+

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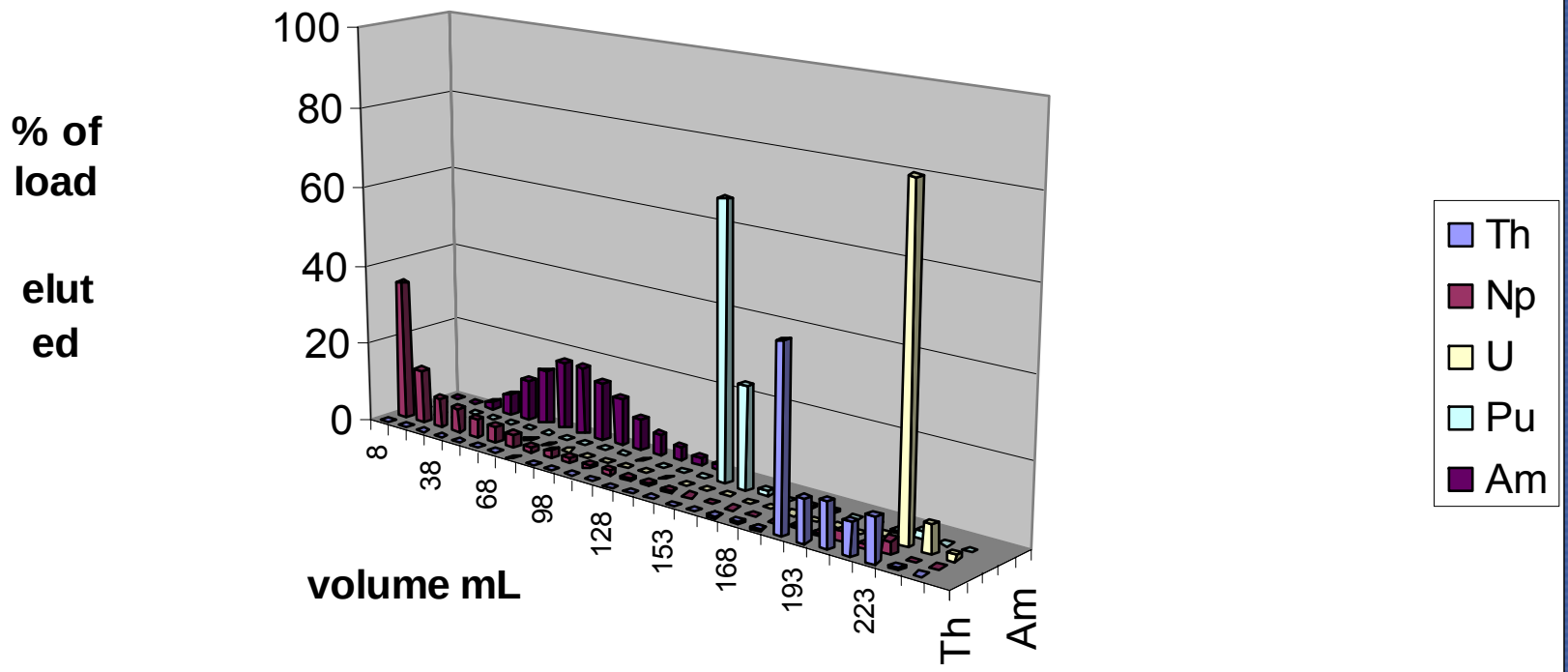
Load: 2M $HNO_3$/0.1M $NaNO_2$
elution (Np + Am): same
Pu strip: 9M HCl/0.02M $Ti^{3+}$
Th strip: 1.5M HCl, U strip: 0.1M bioxalate

TRU (25mm)

## TR6: Elution of actinides from TRU resin with different eluents



# Conclusion

- Soil samples can be destructed with $LiBO_2$ fusion and dissolved in 1M acid.
- Actinides can be preconcentrated with $CaF_2$ or Ca oxalate in acidic media
- Separation of Pu and actinides can be performed on a single, small extraction chromatographic column: TRU (or UTEVA)

| | | | |
|---|---|---|---|
| $LiBO_2$ fusion | $CaF_2$ coprecipitation | Extraction chromatography: TRU | Alpha source |

# *Outcomes during 2005 – 2007 !*

## Published Paper (4 papers)

1. Determination of $^{210}$Po in environmental materials: A review of analytical methodology, App. Radia. Iso., 65 (2007) 267-279
2. Determination of Pu isotope concentrations and isotope ratio by ICP-MS: a review of analytical methodology, J. Anal. At. Spec., 22 (2007) 827-841
3. Current IAEA activities and future plans for the ALMERA network, Environmental Radiochemical Analysis III, RSC publishing, (2007) 207-216
4. Application of an on-line sequential injection system to measurement of Pu, $^{210}$Pb and $^{210}$Po in soil samples, App. Radia. Iso., (in press)

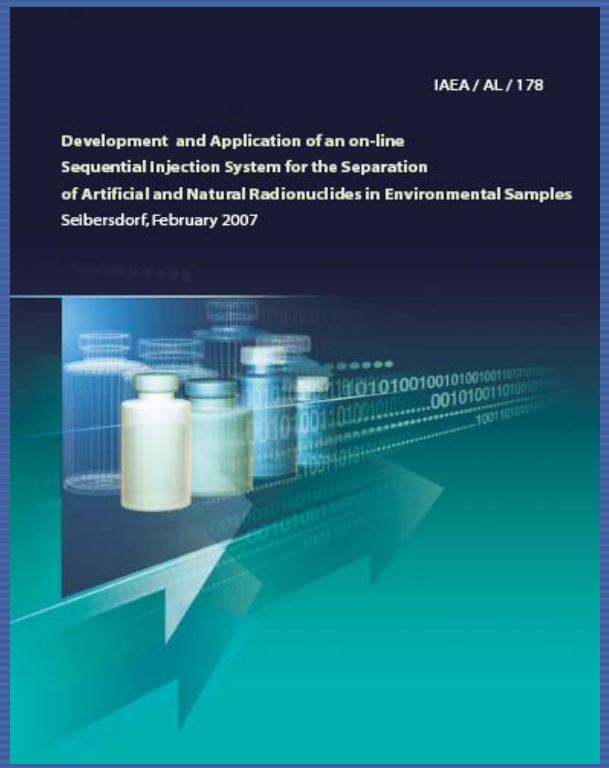
# *Outcomes during 2005 – 2007 !*

## Presentation in International Conference

- Sequential determination of natural radionuclides for characterization of a phosphogypsum candidate IAEA reference material, International conference on Environmental Radioactivity: From measurements and assessment to regulation, Vienna, Austria, April, 2007

## IAEA internal report

- Development and application of an on-line sequential injection system for separation of artificial and natural radionucldes in environmental sample, IAEA/AL/178, 2007

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# Future plans

- Publish rapid method of Pu in soil by alpha-spec and review paper
- Prepare recommended procedures of rapid analysis Pu in soil and $^{210}$Po analysis in water
- Rapid method of $^{90}$Sr in milk
- Review of $^{226}$Ra procedure in environmental samples
- Prepare recommended procedures for rapid analysis of $^{90}$Sr in milk and $^{226}$Ra in soil and water

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# Thank you for your attention

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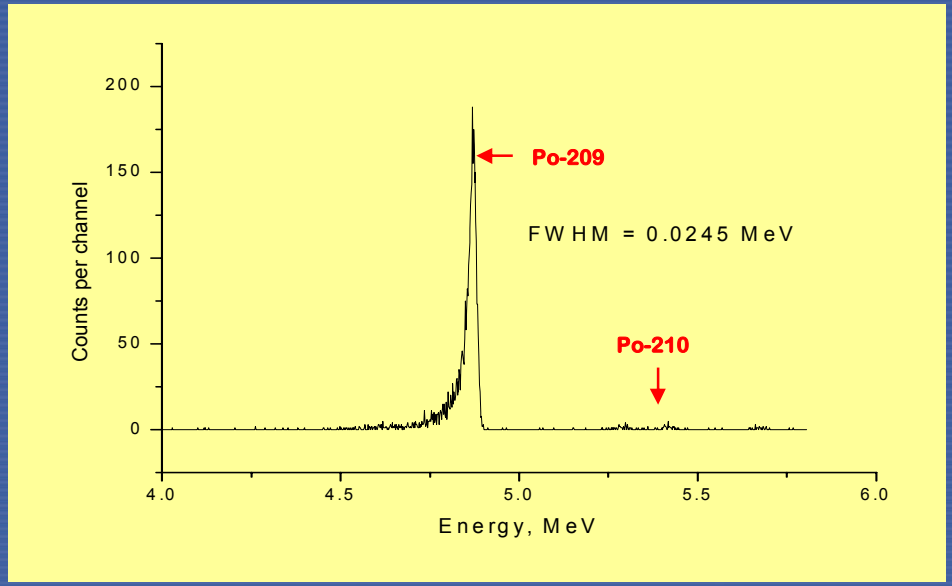
# Comparison of alpha spectra obtained from direct deposition and after chemical separation

a) Alpha spectra of direct deposition source from tap water(2.5 L)




b) Alpha spectra of source prepared after chemical separation from spiked tap water (2.5 L)