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.

Chang Kyu KIM
International Atomic Energy Agency IAEA
Agency’s Laboratories Seibersdorf
Chemistry Unit, A-2444 Seibersdorf
AUSTRIA
Current IAEA Activities for Development of Recommend Procedures of Radionuclides in Terrestrial Environmental Samples

Chang-Kyu Kim
Chemistry Unit, PCI
IAEA - Agency’s Laboratories, Seibersdorf
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?

- Search for relevant papers
- Review paper
- Database of publications

- Comments of experts
- *Analytical procedures for general use
- *Rapid analytical procedure for ALMERA

IAEA publications database/or ALMERA website

*: 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

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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

<table>
<thead>
<tr>
<th>Sample</th>
<th>No. of paper</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>1</td>
</tr>
<tr>
<td>Drinking water</td>
<td>4</td>
</tr>
<tr>
<td>Ground water</td>
<td>3</td>
</tr>
<tr>
<td>Freshwater</td>
<td>6</td>
</tr>
<tr>
<td>Rainwater</td>
<td>4</td>
</tr>
<tr>
<td>Seawater</td>
<td>13</td>
</tr>
<tr>
<td>Soil</td>
<td>6</td>
</tr>
<tr>
<td>Sediment</td>
<td>9</td>
</tr>
<tr>
<td>Coal</td>
<td>1</td>
</tr>
<tr>
<td>Tobacco</td>
<td>8</td>
</tr>
<tr>
<td>Phosphogypsum</td>
<td>6</td>
</tr>
<tr>
<td>Food</td>
<td>9</td>
</tr>
<tr>
<td>Lake fish</td>
<td>1</td>
</tr>
<tr>
<td>Human body</td>
<td>12</td>
</tr>
<tr>
<td>Plant</td>
<td>5</td>
</tr>
<tr>
<td>Biota</td>
<td>13</td>
</tr>
<tr>
<td>Analytical method</td>
<td>29</td>
</tr>
<tr>
<td>Total</td>
<td>130</td>
</tr>
</tbody>
</table>
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, ($^{238}\text{U}^1\text{H}$ at m/z 239)
- Detection limit

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

Cheol-Su Kim, Chang-Kyu Kim, Paul Martin and Umberto Sansone

Received 1st December 2006, Accepted 14th March 2007
First published as an Advance Article on the web 29th March 2007
DOI: 10.1039/b617568f
• 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 $^{239+240}\text{Pu}$ in IAEA reference material (Soil-6) by the on-line SI system

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

* = 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

**U-238**

**Th-230**
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
Outline of Radiochemical Separation of $^{210}$Po in water sample

- Spiked water Sample (1 – 3L)
- Sample Preparation ($\text{MnO}_2$ ppt)
- Po-209
- Solvent Extraction (DDTC)
- Source Preparation (autodeposition, Ag plate)
- Measurement of Po-210 ($\alpha$-spectrometry)

P, Martin et al

N. Vajda et. al
Relative bias and Repeatability (in 10mBq/l of $^{210}$Po)

- DDTC solvent extraction (Repeatability limit: 11.4%)
- Sr-resin extraction chromatography (Repeatability limit: 12%)

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Linearity

(a) Solvent extraction

(b) Extraction chromatography

R = 0.99

Measured activity concentration of Po-210 (Bq)

Added activity concentration of Po-210 (Bq)
Chemical recovery

- **Chemical recovery (%)**

- **No. of reused of Sr resin**

<table>
<thead>
<tr>
<th>Number of sample</th>
<th>1st</th>
<th>2nd</th>
<th>3rd</th>
<th>4th</th>
<th>5th</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical yield (%)</td>
<td>55 - 82</td>
<td>60 - 84</td>
<td>43 - 85</td>
<td>20 - 50</td>
<td>3 - 20</td>
</tr>
</tbody>
</table>
**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 MnO₂ ppt: 1 hr
- Stand MnO₂ ppt: 2 hrs
- Centrifuge MnO₂ ppt and dissolving it with 5 M or 2 M HCl (1% H₂O₂): 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

**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: 13 hrs)  
(Total analysis time: 21 hrs)
## Comparison results of two methods

<table>
<thead>
<tr>
<th>Items</th>
<th>Solvent Extraction</th>
<th>Extraction Chromatography</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linearity</td>
<td>$R = 0.99$</td>
<td>$R = 0.99$</td>
</tr>
<tr>
<td>Repeatability limit (in 3mBq/L)</td>
<td>11%</td>
<td>12%</td>
</tr>
<tr>
<td>Analytical time</td>
<td>13 hrs</td>
<td>21 hrs</td>
</tr>
<tr>
<td>Analytical cost (for only chemical reagent)</td>
<td>5 € (4 samples)</td>
<td>70 € (4 samples, 5 times used)</td>
</tr>
<tr>
<td>Peak resolution</td>
<td>~ 20keV</td>
<td>~ 20keV</td>
</tr>
<tr>
<td>Chemical recovery</td>
<td>&gt; 90</td>
<td>&gt; 80</td>
</tr>
</tbody>
</table>
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 in pH 1
Spectral resolution of $^{209}$Po at different pHs

(a) pH : -1.0

FWHM : 0.0319 MeV
FWTM : 0.0782 MeV

Counts
Energy (MeV)

(b) pH : 0.0

FWHM : 0.0236 MeV
FWTM : 0.0433 MeV

Counts
Energy (MeV)
Variation of the deposition yield of $^{209}$Po with the deposition solution volume

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

in pH 1
### Optimum conditions for auto deposition of Po

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH of deposition solution</td>
<td>1.0</td>
</tr>
<tr>
<td>Deposition time</td>
<td>1.5 h</td>
</tr>
<tr>
<td>Deposition volume</td>
<td>10 mL</td>
</tr>
<tr>
<td>Temperature</td>
<td>90 °C with stirring</td>
</tr>
</tbody>
</table>
Rapid method of Pu in soil by α spectrometry

• Background
  - ICP-MS; expensive, considerable skill operation
  - α spectrometry; most commonly used
  - ALMER 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/NH$_4$I
- 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 microcoprecipitation

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 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, SiO₂, Al₂O₃

Fusion tests in the Fluxer, in Pt dishes:

- **LiBO₂**: some un-attacked SiO₂
- **KF**: not good for refractory oxides
- **pyrosulfate**: not good for silicates
- **KF-sulfuric acid –pyrosulfate**: foaming, spraying
- **KF – LiBO₂**: insoluble salts
- **KF – acid volatilization – LiBO₂**: 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.

<table>
<thead>
<tr>
<th></th>
<th>Oxidation state adjustment</th>
<th>Pu yield %</th>
<th>U yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CP1</td>
<td>-</td>
<td>98</td>
<td></td>
</tr>
<tr>
<td>CP2</td>
<td>-</td>
<td></td>
<td>38</td>
</tr>
<tr>
<td>CP4</td>
<td>Fe(II) N$_2$H$_4$</td>
<td></td>
<td>99</td>
</tr>
<tr>
<td>CP5</td>
<td>Fe(II) N$_2$H$_4$</td>
<td>105</td>
<td></td>
</tr>
</tbody>
</table>

ACIDIC
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.

<table>
<thead>
<tr>
<th>Oxidation state adjustment</th>
<th>Pu yield %</th>
<th>U yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CP8</td>
<td>-</td>
<td>8</td>
</tr>
<tr>
<td>CP11</td>
<td>-</td>
<td>6</td>
</tr>
<tr>
<td>CP6</td>
<td>Fe(II) N$_2$H$_4$</td>
<td>96</td>
</tr>
<tr>
<td>CP7</td>
<td>Fe(II) N$_2$H$_4$</td>
<td>88</td>
</tr>
</tbody>
</table>

LESS ACIDIC
UTEVA Resin: elution of actinides

- Elution of actinides from UTEVA with 3M HNO₃ in presence of persulfate and Fe(III) nitrate

- Elution of actinides from UTEVA with 3M HNO₃ in presence of NaNO₂ and Fe(III) nitrate

- Elution of actinides from UTEVA with 8M HNO₃ in presence of Fe(III) nitrate

- Elution of actinides from UTEVA with 3M HNO₃

Pu is not leaking!
Load: 8M HNO₃/Fe(III)
Pu strip: 9M HCl/0.1M NH₄I
Th strip: 4M HCl
U strip: 0.1M HCl
Am is lost
TRU resin: elution of actinides

TR2: Elution of actinides from TRU Resin with 2M HNO₃/0.001M Fe³⁺

Not adjusted media

Oxidizing media: persulfate

Reducing media: Fe²⁺

TR3: Elution of actinides from TRU resin with 2M HNO₃/0.01M Fe(II) sulfamate

TR4: Elution of actinides from TRU Resin with 2M HNO₃/ammonium persulfate

2M HNO₃
Load: 2M HNO₃/0.1M NaNO₂
elution (Np + Am): same
Pu strip: 9M HCl/0.02M Ti³⁺
Th strip: 1.5M HCl, U strip: 0.1M bioxalate

TR6: Elution of actinides from TRU resin with different eluents

% of load eluted

volume mL

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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).
Outcomes during 2005 – 2007!

Published Paper (4 papers)

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 radionuclides in environmental sample, IAEA/AL/178, 2007
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
Acknowledgement

• Research activity was financially supported under the IAEA sub-programme “Supporting Quality in the Analysis of Terrestrial Environmental sample”

Thank you for your attention

Chang Kyu Kim
c.k.kim@iaea.org
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)