Automation of the radiochemical procedures for the sequential separation of radionuclides

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I. Design and fabrication of an Automated Sequential Radionuclide Separator
   ✓ ASRS hardware and software

II. Characterization of the ASRS
   ✓ Pump calibration
   ✓ Flow rate characterization
   ✓ Dead volume and memory effect

III. Optimization of an automated sequential radiochemical procedures
    ✓ Tandem column arrangement: TRU resin and Sr-spec resin
    ✓ Flow rate effects on method efficiency: separation of Fe and Sr

IV. Application of the ASRS
    ✓ Determination of $^{55}$Fe and $^{90}$Sr by ASRS and liquid scintillation counter
WHY Rapid analysis & Automation?

- Many samples in an emergency situation
- Repeated process in radiochemical separation
- Use of toxic chemicals in RNs separation
- Labor-intensive radiochemical process
- Human error under long-period repeated works
- Slow and time-consuming under gravity flow
- Deterioration of reproducibility in a vacuum manifold
- To increase sample throughput and reproducibility
- To reduce sample preparation costs
- To improve worker safety
- To provide accurate and timely analytical results
Conventional method & Rapid method?
On the radiochemical separations

Classical method
Gravity-feed ion exchange

Gravity flow rate

Rapid method
Pump or Vacuum feed ion exchange

Control of flow rate

Enhance the flow rate
Separation systems for enhancing the flow rate

Eichrom: Vacuum Box System

- Enhanced flow rate, but manual process
- Efficient for batch processing
- Sample through-put is limited by the labor force and individual skill sets
- Exposed to the open sources of radioactivity
What do you need for translating manual methods into automated methods?

Eichrom: Vacuum Box System
Enhanced flow rate, but manual process

Automation

Solenoid valve - Reagent and sample selection

Digital I/O Board - Interface

PC based - Control Software
Simultaneous Determination of Hard-to-Measure Radionuclides: Extraction Chromatography, Mass Spectrometry & Radiometry

- TEVA
- UTEVA
- DGA
- Sr-Spec
- TRU

Th/Pu/Np → U → Am/Cm/REEs/Y → Sr/Pb/Po → Fe/Am/Pu

- Alpha Spectrometry
- Mass Spectrometry
- LS & Cerenkov counting

- Application: $^{55}\text{Fe}$ and $^{90}\text{Sr}$
- Sr-Spec resin
- TRU resin
- Liquid Scintillation Counting

Automation
- Design
- Fabrication
- Characterization
- Optimization
Design of an automated radionuclide separation system:
Sequential separation by single column arrangement: 1 sample

- 1 sample
- 1 column
- Pu, Th, Np
- Load
- TEVA
- Pu, Th, Np
- Waste

**Automation**

- Solid red lines: fluid line tubing
- Dotted blue lines: signal communication lines

- 6 way valve: 1ea (20)
- 2 way valve: 1ea (42)
- 4 way valve: 1ea (70)
- 1-channel pump: 1ea (41)
- Digital I/O board: 1ea (5)
- PC-control software: 1ea (4)
Design of an automated radionuclide separation system: Sequential separation by tandem column arrangement: 1 sample

 Automation

- Solid red lines: fluid line tubing
- Dotted blue lines: signal communication lines

- 6 way valve: 2ea (20,30)
- 2 way valve: 2ea (42,52,60)
- 4 way valve: 2ea (70,80)
- 1-channel pump: 2ea (41,51)
- Digital I/O board: 1ea (5)
- PC-control software: 1ea (4)
Design of an automated radionuclide separation system: Sequential separation by tandem column arrangement: 4 samples

- Solid red lines: fluid line tubing
- Dotted blue lines: signal communication lines

- 6 way valve: 2ea (20,30)
- 4 way connector: 2ea (40, 50)
- 2 way valve: 8ea (41~44,51~54)
- 4 way valve: 8ea (71~78)
- 1-channel pump: 8ea (11~18)
- Digital I/O board: 1ea (20)
- PC-control software: 1ea (19)
Design of an automated radionuclide separation system:
Algorithm used to the source code for executing the automated protocol

Signal and fluid connection of the ASRS

Algorithm to control the ASRS

Choose single or tandem column arrangement

Choose number of operating columns

Choose number of steps

Choose a process at each step
Fabrication of an automated radionuclide separation system:

*Control software of ASRS*

System control software: **VIRTUAL INSTRUMENT**

Graphical User Interface: easy to learn and use the software
Fabrication of an automated radionuclide separation system:  
**Conceptual design of ASRS**

- **Automated column-based extraction chromatography**
- **2 RNs**: 8 samples in parallel with a single column arrangement
- **5 RNs**: 4 samples in parallel with a tandem column arrangement
- **PC control**: system software (LabVIEW) for instrument control
Automated Sequential Radionuclide Separator: Fabrication of ASRS

Design of a solenoid valve driver circuit board to actuate solenoid valves

- Solenoid valve ON: connect 24V DC
- Solenoid valve OFF: disconnect 24V DC

To prevent overheating valves: 24V → 8V

Power Supply → Digital I/O Board → PC-Control Software

- Switching 24V DC
- V (volt): 24 volt
- V (volt): 8 volt

$t$ (min)
Automated Sequential Radionuclide Separator: Fabrication of ASRS

Design of a peristaltic pump driver circuit board to control peristaltic pumps

- Pump Board 1
- Pump Board 2

**Pump calibration function:**
* Flow rate \( f \) (mL/min) = \( a \) (mL/min/volt) * voltage \( V \), volt + \( b \) (mL/min)

**Input parameters:** Flow rate \( f \) (mL/min), Volume (mL)

**Pump working time** \( t \) (min): calculated by input parameters
* \( t \) (min) = Volume/Flow rate

**Pump speed control** (volt): Calculated by pump calibration function
* \( V \) (volt) = \( (f - b)/a \)

- Digital I/O Board
- Analog I/O Board
- Power Supply
- PC-Control Software

Switching 24V DC
Applying 0~5V DC

On
OFF

0~5 V

- 24 V DC

on/off
0~5 V
KAERI development history of Automated Radionuclide Separator

MARS Sr-90, 2007~2009

MARS Tc-99, 2008~2010

ASRS-two pumps, 2012~2014

Minimized flow difference between the pumps
Slow deterioration of the pump tubing

ASRS-eight pumps, 2014~2015

Commercialized models, 2016~

✓ The peristaltic pump has a 4-channels head
✓ Flow rate differences between the channels
An automated separation system developed by KAERI: Modular Automated Radionuclide Separator for Sr-90

- Modular type system: control module, pump module, valve module, column module
- Four samples in parallel
- User friendly system software: Virtual Instrument
- Input parameters: volume, flow rate, reagent number in conditioning, rinsing, loading and elution steps

**MARS Sr-90 Prototype**

Rapid determination of radiostrontium in milk using automated radionuclides separator and liquid scintillation counter

Kun Ho Chung · Hyuncheol Kim · Jung Mysung Lim · Young-Yong Ji · Goun-Sik Choi · Mun Ja Kang

Received: 1 September 2014 / Published online: 19 September 2014 © Akadémiai Kiadó, Budapest, Hungary 2014

Abstract A modular automated radionuclide separator for $^{90}$Sr (MARS Sr-90) has been developed for the rapid and reproducible isolation of radiostrontium. The automated radiochemical method for separation and purification of $^{90}$Sr in milk was developed and verified in the literature [1-8]. Both $^{90}$Sr and $^{90}$Y, produced by the fission reaction of nuclear fuel in a nuclear reactor, are beta emitters that require radiochemical separation for radiometric analysis. The conventional methods for the determination of radiostrontium in milk are time consuming sample preparation.
An automated separation system developed by KAERI:

**Modular Automated Radionuclide Separator for Tc-99**

- Modular type system: control module, pump module, valve module, column module
- User friendly system software: Virtual Instrument
- GM counter: monitor and select of $^{99m}$Tc/$^{99}$Tc from the sample
- GM counter signal: Used to switch the 3W-FDV

Chung *et al.*, Appl. Radat. Isot., 2013, 81, 57-61
Automated Sequential Radionuclide Separator: 
*Developed ASRS*

System Design Specification
Automated Sequential Radionuclide Separator: Developed ASRS

System Configuration

- The ASRS consists of three parts: ASRS-CS, ASRS-MC, ASRS-SS.
- The ASRS-CS means “Automated Sequential Radionuclide Separator-Control Software.
- The ASRS-MC means “Automated Sequential Radionuclide Separator-Main Controller, which is built in ASRS-SS.
- The ASRS-SS means “Automated Sequential Radionuclide Separator-Sequential chromatographic Separator.
System Configuration

The ASRS-SS consists of five parts: Reagent bottle part (column #1~4 & column #5-8), Sample tube part (column #1~4 & column #5-8), Column part (column #1~4 & column #5-8), Pump part (pump #1~4 & pump #5-8), Elution tube part (column #1~4 & column #5-8).
Automated Sequential Radionuclide Separator: Developed Control software of ASRS: VIRTUAL INSTRUMENT

Control Software Configuration
The ASRS-CS consists of three parts: Pump calibration mode, Calibration parameter calculation mode and Execution mode. **Input parameters:** Flow rate, Volume, Reagent, Tandem column mode, column number, elution bottle selection
Characterization of the ASRS:

**Pump Calibration of ASRS**

- Flow rate characterization of the ASRS: excellent precision, accuracy and linearity
- Measured by weighing the masses of deionized water

### Flow rate characterization

- **Pump calibration_left module**
  - Equation: \( y = 1.8077x + 0.0414 \)
  - \( R^2 = 1 \)

- **Pump calibration_right module**
  - Equation: \( y = 1.7689x + 0.0283 \)
  - \( R^2 = 1 \)

### Flow rate characterization

<table>
<thead>
<tr>
<th>Set flow rate (mL/min)</th>
<th>Measured flow rate (mL/min)</th>
<th>std</th>
<th>rsd (%)</th>
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<tbody>
<tr>
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Characterization of the ASRS:  
*System dead volume and memory effect of ASRS*

- Line tubing was completely washed by 4 dead volume with 3M HNO$_3$.

- **Single column arrangement**
  - Dead volume = 3.5 mL
  - Rinsing solution: 3M HNO$_3$

- **Tandem column arrangement**
  - Dead volume = 5.5 mL
  - Rinsing solution: 3M HNO$_3$
Optimization of an automated sequential radiochemical procedures:  
*Tandem column arrangement: TRU and Sr-spec resin*

Sequential analysis of Fe & Sr in water: a tandem column arrangement

![Diagram of the tandem column arrangement]

- **Load the sample**
  - TRU Resin
  - Sr-Spec Resin

- **Conditioning**
  - 20 mL, 8M HNO₃

- **Loading**
  - 20 mL, Sample

- **Rinsing-1**
  - 20 mL, 8M HNO₃

- **Rinsing-2**
  - 6 mL, 8M HNO₃

- **Elution**
  - Fe: 20 mL, 2M HNO₃
  - Sr: 20 mL, D.I. water

Sample tubes: Fe, Sr, U, Th, Ni, Ba

Reagent bottles

TRU resin 2 mL B.V. Cartridges

Sr-Spec resin 2 mL B.V. Cartridges

Elution tubes: Fe

Elution tubes: Sr
Optimization of an automated sequential radiochemical procedures: *Tandem column arrangement: TRU and Sr-spec resin*

Flow rate effects on the method efficiency: separation of stable Fe & Sr, measured by ICP-OES
Optimization of an automated sequential radiochemical procedures: Tandem column arrangement: TRU and Sr-spec resin

Flow rate effects on the method efficiency: separation of Fe & Sr

- Sr recoveries exceeded 94%
- Fe recoveries showed 100%
- Over a wide range flow rate (1~5 mL/min)
- Highly reproducible (r.s.d. : less than 2%)
- In-house column packing: 2 mL dry pack cartridge
- Sufficient removal of interferences
Application of the **ASRS**: Determination of $^{55}$Fe and $^{90}$Sr by ASRS and LSC

- **Sample tubes**
  - Fe, Sr, U, Th, Ni, Ba: ~ 1mg
  - $^{55}$Fe: 13.99 Bq
  - $^{90}$Sr: 13.60 Bq

- **Procedure Steps**
  1. **Conditioning**: 20 mL, 8M HNO$_3$
  2. **Loading**: 20 mL, Sample
  3. **Rinsing-1**: 20 mL, 8M HNO$_3$
  4. **Rinsing-2**: 6 mL, 8M HNO$_3$, 6 mL, 8M HNO$_3$
  5. **Elution**: 20 mL, 2M HNO$_3$, 20 mL, D.I. water

- **Tandem column mode**
- **TRU resin**: 2mL B.V.
- **Sr-spec resin**: 2 mL B.V.
- **Flow rate**: 3 mL/min
- **Separation time**: 29 min
Application of the **ASRS**:
Determination of $^{55}$Fe and $^{90}$Sr by ASRS and LSC

Performance test of **ASRS**: simultaneous measurement of $^{55}$Fe & $^{90}$Sr in spiked sample

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**LSC Samples**

- $^{55}$Fe:
  - 1 mL 2M H$_3$PO$_4$
  - 2 mL D.I. water
  - 15 mL Ultima Gold AB

- $^{90}$Sr:
  - 10 mL 0.1M HNO$_3$
  - 10 mL Ultima Gold AB

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**Sample tubes**

- Fe, Sr, U, Th, Ni, Ba: ~ 1mg
- $^{55}$Fe: 13.99 Bq
- $^{90}$Sr: 13.60 Bq
- Tandem column mode
- TRU resin: 2mL B.V.
- Sr-spec resin: 2 mL B.V.
- Flow rate: 3 mL/min
- Separation time: 29 min

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### (n=3) Chemical yield (%) Activity Relative vias (%)

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<tr>
<td>std</td>
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<td>1.14</td>
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<tr>
<td>rsd(%)</td>
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<td>8.05</td>
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### (n=3) Chemical yield (%) Activity Relative vias (%)

<p>| | | | |</p>
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<thead>
<tr>
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</thead>
<tbody>
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<td>14.00</td>
<td>2.9</td>
</tr>
<tr>
<td>std</td>
<td>1.4</td>
<td>0.59</td>
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<tr>
<td>rsd(%)</td>
<td>1.6</td>
<td>4.21</td>
<td></td>
</tr>
</tbody>
</table>
Closing Remarks: Automated Radiochemical Separation!!!

- **ASRS**: fully automated column based extraction chromatography
- **Flowrate characterization**: excellent accuracy, precision and linearity, minimized flow difference between the 8 pumps (RSD: < 1%)
- **System memory effect**: washing the tubing with 4 dead volume
- **Reliable and reproducible**: recovery (>94%), relative bias(<3%), RSD (< 2%, n=3)
- **High-throughput**: simultaneous 4 samples, up to 5 RNs, within 1 hour
- **Rapid and safe**: compared to conventional methods
- **Less labour-intensive**: fully automated radiochemical procedures
- **Powerful and convenient tool**: an automated chemical separation and purification of RNs at trace levels in environmental samples
- **Suitable for a routine and an emergency response**: Rapid, reliable, high-throughput
Thank you for your attention!