

Video Article

Automated ^{90}Sr Separation and Preconcentration in a Lab-on-Valve System at Ppq Level

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Abstract

A quick, automated and portable system for the separation and determination of radiostrontium in aqueous samples, using Sr-resin and multi sequential flow injection analysis, has been developed. The concentrations of radioactive strontium were determined by flow scintillation counting, allowing for on-line and also on-site determination. The proposed system can determine radioactive strontium at industrial relevant levels without further modification using overall analysis time of less than 10 min per aqueous sample. The limit of the detection is $320 \text{ fg}\cdot\text{g}^{-1}$ (1.7 Bq/g).

Video Link

The video component of this article can be found at <https://www.jove.com/video/57722/>

Introduction

About 150 commercial nuclear power plants (NPP) are undergoing decommissioning, but the total number of nuclear facilities is much greater if research and reprocessing facilities are taken into consideration¹. Decommissioning of nuclear facilities is very costly and involves transport and off site measurement of contaminated material. Savings are possible by adopting on-site and flexible measurement techniques¹. There is therefore an urgent need for rapid on site analytical methods supporting the decommissioning of old nuclear facilities. Gamma-emitters can be easily and selectively determined using gamma-spectroscopy, but there is a deficiency in on-site analytical methods for the hard-to-measure (HTM) radionuclides². Among the HTM, ^{90}Sr is of great interest due to its toxicity and high energy emission. Its determination is time consuming and requires the separation from interferences and quantification using LSC or spectroscopic methods^{3,4,5,6,7,8,9,10,11,12,13}.

Standard radiochemical methods are time-consuming and often require repetitions to obtain an adequate yield of strontium. Therefore, there is an urgent need for faster and accurate methods. Besides the standard separation protocols, flow injection techniques are applied in the purification and/or pre-concentration of radioisotopes^{5,14,15}. Lab-on-Valve (LOV) devices are a further development in flow techniques. They are programmable, flow-based platforms with different coupling modes and exhibit high versatility¹⁶. Such devices allow the automatic separation and pre-concentration of the analytes prior to the detection, thus increasing reproducibility and repeatability^{8,17,18,19}. LOV systems coupled to multisyringe flow pumps have been widely used for the detection of radionuclides, due to the minimization of the reagent consumption and waste generation^{8,10,17,18,19,20}. Nevertheless, reported studies regarding online detection at ultra-trace levels are sparse^{8,17}.

On-site measurements of radioactive materials have many benefits and advantages, but there is no application of flow scintillation to ^{90}Sr monitoring. Basically, quantification is achieved using an online detector that mixes the eluate coming from the LOV device with the scintillating cocktail^{11,21,22}. The mixture is then pumped through the counting cell and measurement is made using paired photomultipliers. Due to the small volume of the cell, the measurement time is in the seconds scale.

The aim of this research is the development of a fully automated method for on-line strontium detection over a large working range, covering both environmentally relevant concentrations and also those found in nuclear industry waste streams. The platform is mobile and can be mounted in a vehicle to perform on-site analysis of aqueous samples.

Protocol

Note: Solutions were prepared from high-purity water ($18.2 \text{ M}\Omega \text{ cm}$) using devices designed for ultratrace analysis. Nitric acid was purified using a quartz sub-boiling distillation unit. Both the water purification system and the sub-boiling distillation unit were operated in a clean room.

Caution: ^{90}Sr is acutely toxic and carcinogenic. Appropriate safety practices are essential when performing the experiments, including both engineering control systems and personal protective equipment.

1. Experiment Preparation

Note: A detailed description regarding the software architecture and its functionalities can be found elsewhere²³.

1. Connect the Modular Valve Position exit port to the entry port of the radio flow detector.
2. Connect the Trigger line to selected detector.
3. Ensure that the LOV ports are properly connected. Ensure that adequate volumes of working solutions are available for the entire protocol and that liquid sampling tubing will remain submerged.
4. Ensure that the Autosampler is on, start the autosampler software, and via the software interface, initialize the autosampler. Click the **Initialize** button to generate the communication between the apparatus and the PC.
5. Ensure the AutoRAD software has been started, check the communication ports using the options tab and initialize the software via the user interface. Refer to Discussion section for more details regarding the software graphical interface.
6. Ensure that the analysis sequence is programmed in the detector Software. Program view sequences using the **Method editor** tab in the AutoRAD software, by entering the number of steps needed and the tasks and speed for each device.
Note: A detailed description of the software operation can be found in previous publication²³.
7. Consult the local radioprotection officer and employ the radioprotection measurements needed for the complete procedure using ⁹⁰Sr.

2. System Cleaning

1. Load 10 mL of 18.2 MΩ cm water from the flask to the syringe at 90 mL·min⁻¹. Ensure that the syringe valve position is set to the **In** position for this step. In this position, loading occurs directly to the syringe and not through the LOV.
2. Drop the water to the waste via the holding coil at a flow rate of 90 mL·min⁻¹.
3. Load 3 mL of ethanol to the holding coil at a flow rate of 3 mL·min⁻¹. Set the syringe valve position to **Out**.
4. Drop the ethanol to the detector coil at a flow rate of 3 mL·min⁻¹.

3. Load Resin to the LOV

1. While stirring the resin suspension in water (12 mg·mL⁻¹), pick up 3 mL via the LOV. Set the flow to 3 mL·min⁻¹
2. Drop the resin suspension into the column channel at a flow rate of 1.2 mL·min⁻¹
3. Clean the holding coil and drop the resin residues onto the column channel. For this, load 9 mL of 18.2 MΩ cm water from the flask to the syringe at a flow rate of 90 mL·min⁻¹. Ensure that the syringe valve position is in the **In** position. Drop the water to the waste via the holding coil at a flow rate of 3 mL·min⁻¹.

4. Analysis Sequence

1. Column conditioning
 1. Load 2 mL of HNO₃ (4 M) via the LOV to the holding coil. Set the flow to 6 mL·min⁻¹.
 2. Drop the HNO₃ onto the column at a flow rate of 1.2 mL·min⁻¹.
2. Sample loading and elimination of interferences
 1. Load sample (1.3 mL) from the autosampler to the holding coil at a flow rate of 6 mL·min⁻¹.
 2. Drop the sample onto the column at a flow rate of 1.2 mL·min⁻¹.
 3. Load 0.5 mL of HNO₃ (4 M) to the holding coil at a flow rate of 6 mL·min⁻¹.
 4. Rinse the column with 0.5 mL of HNO₃ (4 M) to elute matrix interferences at a flow rate of 1.2 mL·min⁻¹.
3. Elution of the sample and measurement
 1. Load 5 mL of 18.2 MΩ cm water to the holding coil at a flow rate of 6 mL·min⁻¹.
 2. Trigger the detector. Set the flow rate of the scintillation liquid to 2 mL·min⁻¹ in the detector software. Set the dwell to 10 s. The sample coil has a volume of 2 mL.
 3. Rinse the column.
4. rinsing of the sample probe and holding coil
 1. Load 0.6 mL of HNO₃ (1%) to the holding coil at a flow rate of 6 mL·min⁻¹.
 2. Load 0.6 mL of air to the holding coil at a flow rate of 6 mL·min⁻¹.
 3. Discharge 1.2 mL of the mixture to the waste.
5. Resin replacement
 1. Load 0.2 mL of ethanol to the holding coil at a flow rate of 3 mL·min⁻¹.
 2. Rinse the column with 0.2 mL of ethanol at a flow rate of 1.2 mL·min⁻¹.
 3. Flush the column channel with 0.5 mL of water at a flow rate of 0.45 mL·min⁻¹.
 4. Discharge the used resin to the waste.

Representative Results

The fully automated AUTORAD platform operated by homemade LabVIEW-based software has been developed and implemented (Figure 1). The software allows sufficient flexibility for daily operation in a user-friendly environment (Figure 2). The versatility of the platform has been also demonstrated by coupling it to different detectors (Figure 3). The applicability of the method has been demonstrated in aqueous samples spiked with a ^{90}Sr standard (Figure 4). The parameters linearity, linear range, limit of detection (LOD) and repeatability have been evaluated (Figure 5).

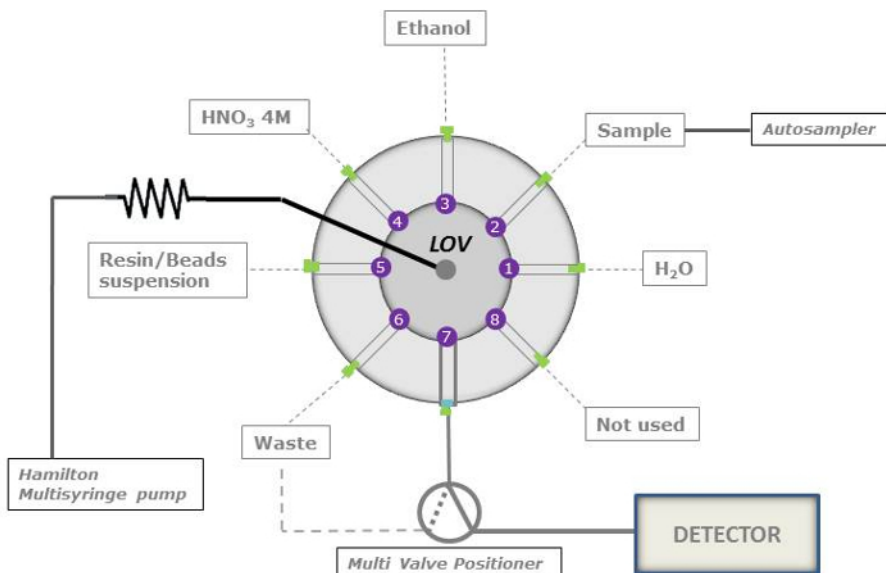


Figure 1. Schematic representation of the AutoRAD system showing the port configuration and reagents used. The central port is connected to the syringe pump via the holding coil (10 mL); the methacrylate LOV was fabricated in house. [Please click here to view a larger version of this figure.](#)

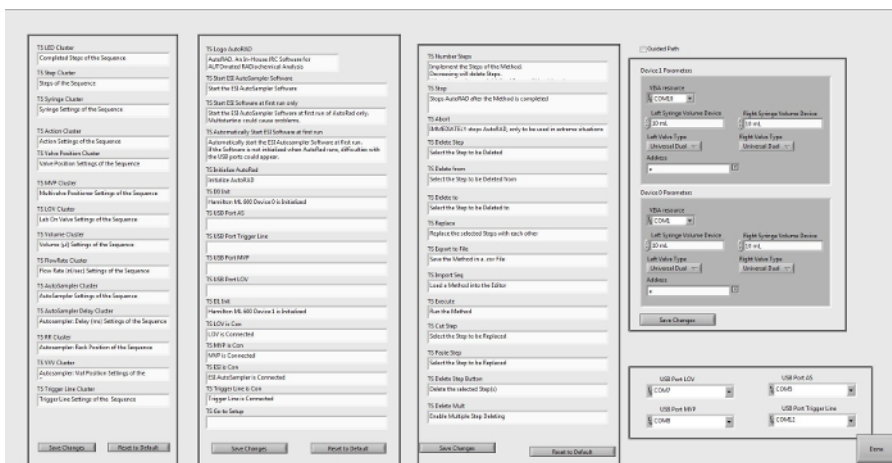


Figure 2. AutoRAD Software options menu. The bottom right corner area shows the assigned ports. Via the scroll down menu, the user is able to make changes in the assignment. [Please click here to view a larger version of this figure.](#)

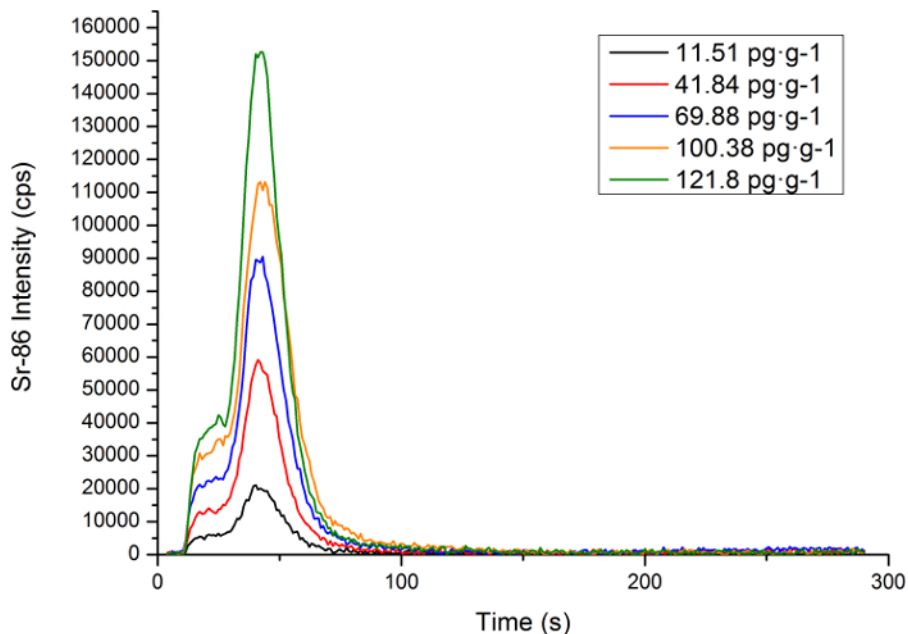


Figure 3. ^{86}Sr elution peaks using an Inductively coupled plasma mass spectrometry (ICP-MS) as a detector. Strontium is eluted quantitatively from the column during the first 100 s of the elution. [Please click here to view a larger version of this figure.](#)

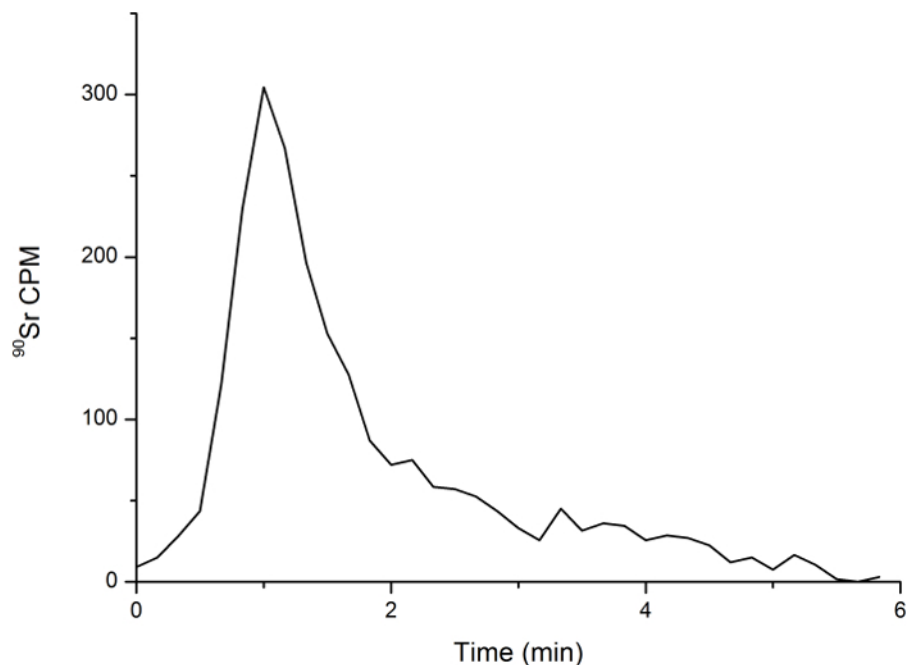


Figure 4. $34.5 \pm 1 \text{ Bq } ^{90}\text{Sr}$ ($6.6 \text{ pg}\cdot\text{g}^{-1}$) elution peak using β -RAM 5 as detector. The residence time in the coil was 40 s. The overall recovery rate of the proposed methodology for ^{90}Sr is $70\% \pm 5\%$. [Please click here to view a larger version of this figure.](#)

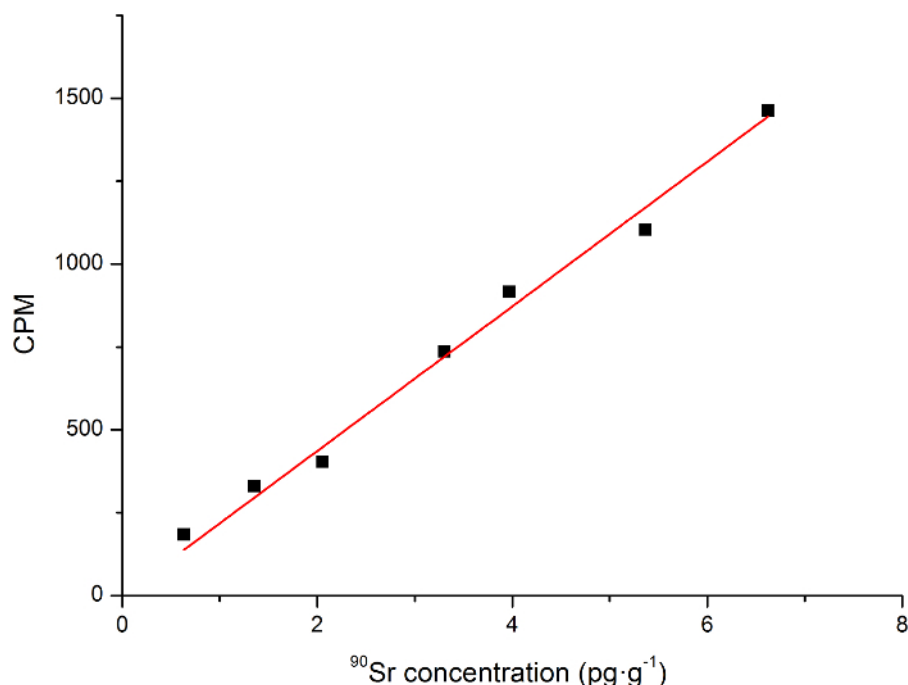


Figure 5. Calibration curve for the count rate versus the concentration of radiostrontium. A good linearity was obtained ($R^2 = 0.997$). The detection limit was calculated as $320 \text{ fg} \cdot \text{g}^{-1} \pm 5$ (1.7 Bq) by three point three times standard deviation of the blank. [Please click here to view a larger version of this figure.](#)

Discussion

Radiological characterization and protection are critical issues during all phases of a nuclear facility life cycle. The need for radionuclide determination during the decommissioning of nuclear facilities requires continuous improvement of analytical procedures. This entails the enhancement of selectivity and sensitivity, and shortening the analysis time. The AUTORAD prototype fulfils these requirements. In addition, the prototype is portable and allows on-site determination. The proposed automated on-line method was successfully applied for the determination of ⁹⁰Sr activity in aqueous samples.

Figure 1 shows a schematic diagram of the AutoRAD system. Communication with the prototype was achieved using the commercial graphical programming language LabVIEW 2014. The Virtual Instrument Software Architecture (VISA) mode for configuring, programming and controlling interfaces was deployed. **Figure 2** shows the graphical user interface screen where the port configuration can be verified prior to system initialization. The VISA mode is independent on the operating system and program environment, so it provides exceptional versatility. The basic structure and features of the developed software have been widely discussed in previous publication²⁴. Improvements have been achieved by controlling the burettes by the PC using an RS232 interface, thus allowing enhanced control of both burettes simultaneously and the possibility to perform measurements in stop flow mode. In contrast, the RS232 connection reacts quickly when the system backpressure increases. This can lead to system error and measurement stop. Therefore, special attention has to be paid in the process of resin loading and ionic strength of the samples.

The optimization of the experimental conditions was achieved in a set of experiments using the strontium stable isotope ⁸⁶Sr as a surrogate for the radioactive ⁹⁰Sr, and by coupling the AUTORAD system to an ICP-MS rather than a beta detector system. **Figure 3** shows the ICP-MS ⁸⁶Sr elution profiles. The obtained ⁸⁶Sr elution profiles are in full agreement with previously reported results for total strontium using low pressure separation devices²⁵, and have been blank subtracted. The least squares linear regression method was used to generate a fit for the purpose curve which does not introduce an extra uncertainty component. The linearity obtained was 0.995, with *p*-values less than the significance level. The LOD of $2 \text{ pg} \cdot \text{g}^{-1}$ was determined by repeated measurements of the blank according to Currie²⁶. The reproducibility of the method, based on the relative standard deviation of the peak area calculated on the basis of three repeated runs, was always less than 4% in the range of 10 to $120 \text{ pg} \cdot \text{g}^{-1}$. The shoulder witnessed in the elution profiles is most likely an artefact due to non-optimal packing of the column in the automated AUTORAD configuration.

Figure 4 shows the ⁹⁰Sr profile using the the radio flow detector. The AUTORAD system is able to effectively separate ⁹⁰Sr in aqueous samples.

Figure 5 shows the dependence of the ⁹⁰Sr concentration with the signal is linear in the range of interest. The derived detection limit is in the $\text{fg} \cdot \text{g}^{-1}$ range, enabling, without further modification, the determination of radiostrontium in nuclear decommissioning and waste characterization samples. Reproducibility of the method, using the flow scintillation detector and based on the relative standard deviation of the peak area, is around 30% in the studied concentration range. The current set-up of the prototype, however, limits its application to environmental samples, essentially due to the short time counting in the detector. Furthermore, complex matrices might saturate the resin in the mini column.

The stopped-flow technique, where both Hamilton and radio flow detector pump are stopped during the measurement, will be implemented. This feature will improve the sensitivity by extending the residence time in the largest part of the sample zone within the flow cell. Thus, a statistically meaningful signal is accumulated before the sample exits the detector. This approach will improve both the counting statistics and the detection

limits. In addition, a new application is being developed including an additional ion-exchange mini-column for the removal of matrix components that could affect the retention and separation of different radionuclides in complex matrix samples.

Disclosures

The authors have nothing to disclose.

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