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Determination of Parts-Per-Trillion Concentrations of Strontium by Pre-Concentration with Ion Chromatography and Suppressed Conductivity Detection

INTRODUCTION

Nuclear power plants are an important source of electrical energy and are responsible for producing nearly 29% of the world's electricity.¹ The heat generated in nuclear power plants to generate electricity is created by the fission of uranium or plutonium to radioactive isotopes, including the strontium ⁹⁰Sr and ⁸⁹Sr isotopes.^{2,3} The nuclear power industry monitors the primary coolant for the effluents ⁹⁰Sr and ⁸⁹Sr to ensure the radioactive fission products meet the nuclear power regulatory requirements and to study the behavior of isotopes within the primary coolant.^{2,3} Although both isotopes are strong β -particle emitters, ⁹⁰Sr has the longer half life ($T_{1/2} = 28.9$ y), and therefore is a greater concern.⁴

⁹⁰Sr is a health concern because it is chemically similar to calcium and therefore readily metabolized by the body. Calcium is displaced by ⁹⁰Sr in bones and teeth resulting in long term storage and exposure to the radioisotope. This is especially a concern with children, but ⁹⁰Sr has also been associated with thyroid cancer and leukemia in all ages.⁴ Because of these health concerns and regulatory requirements, it is important to accurately determine trace concentrations of radioactive strontium.

In this AN, we describe the determination of parts-per-trillion (ng/L) concentrations of non-radioactive strontium in deionized water using pre-concentration

followed by cation-exchange chromatography with an electrolytically generated methanesulfonic acid (MSA) eluent and suppressed conductivity detection. IC appears superior to the conventionally used methods in speed, reliability, and exposure to radioactive contaminants.

A 5 μ m 3 \times 150 mm IonPac[®] CS12A column was used in this application, which requires a slower flow rate than a typical 4 mm column and therefore results in lower eluent consumption and waste. The smaller particle size provides increased peak efficiencies of inorganic cations, and thus results in lower detection limits. In this method, an AXP auxiliary pump concentrates a 25 mL sample onto an IonPac TCC-XLP1 (6 \times 16 mm) concentrator column that is eluted at 0.5 mL/min by 30 mM MSA onto the IonPac CS12A column. A Reagent Free[™] Ion Chromatography (RFIC-EG[™]) system produces the eluent, thereby reducing labor, and improving consistency. In this application, we discuss the system noise, the estimated limits of detection, linear calibration response of peak area, and the chromatography of the system blank and trace concentrations of non-radioactive strontium. Radioactive materials were not used to develop this application. However, this application is intended for the chromatography of both non-radioactive and radioactive strontium and can be used in conjunction with fraction collection and liquid scintillation counting to determine ~10–100 pg/L concentrations of ⁹⁰Sr.^{2,3}

EXPERIMENTAL

Equipment

Dionex ICS-2000 RFIC-EG™ system with EGC II MSA (P/N 058902) with Continuously Regenerated Cation Trap Column II (CR-CTC II, P/N 066262)^a

AXP Metering Pump (Dionex P/N 063973) with RS-232 modular cable (P/N 061046) and a RJ-11 adapter (RJ-11 to DB9 adapter, P/N 061045 or RJ-11 to DB25 adapter, P/N 061047)

Pressurized Sample Vessel (Dionex P/N 037460)

Chromleon® 6.8 Chromatography Data System

^aThis application can be performed on any other RFIC-EG system.

Consumables

225 mL polystyrene tissue culture flasks (VWR P/N 29186-199)

PEEK™ Tubing:

Red (0.127 mm or 0.005 in i.d., P/N 052310 for 5 ft) tubing, used for liquid line connections from injection valve to the guard and analytical columns, cell, and suppressor.

Black (0.25 mm or 0.01 in i.d., P/N 052306 for 5 ft) tubing, used for liquid line connections on the concentrator column.

Yellow (0.76 mm or 0.003 in i.d., P/N 052301 for 5 ft) tubing, used for system backpressure loops on both pumps.

Orange (0.51 mm or 0.02 in i.d., P/N 052309 for 5 ft) tubing, used for the sample transfer line and eluent waste lines.

Backpressure loop for suppressor, red PEEK (P/N 45878)

REAGENTS AND STANDARDS

Deionized water, Type 1 reagent-grade, 18.2 MΩ-cm resistivity, freshly degassed by ultrasonic agitation and applied vacuum

Use only ACS reagent grade chemicals for all reagents and standards.

Strontium chloride hexahydrate (Sigma-Aldrich, P/N 255521)

IonPac® Combined Six Cation Standard-II (Dionex, P/N 046070)

CONDITIONS

Columns: IonPac CS12A 5-μm Analytical (3 × 150 mm, P/N 057185)

IonPac CS12A 5-μm Guard, (3 × 30 mm, P/N 057184)

Eluent: 30 mM Methanesulfonic acid (MSA)

Eluent Source: EGC II MSA with CR-CTC II

Flow Rate: 0.5 mL/min

Column

Temperature: 30 °C

AXP Pump

Flow Rate: 2.5 mL/min

Inj. Volume: 25 mL

Concentrator: IonPac TCC-XLP1 (6 × 16 mm, P/N 063889)

Detection: Suppressed conductivity, Cation Self-Regenerating Suppressor® CSRS® 300 (2 mm, P/N 064557), recycle mode, 44 mA

Background: <0.5 μS

Noise: <0.5 nS

System

Backpressure: 2200 psi

Run time: 7 min + 10 min required for sample pre-concentration

PREPARATION OF SOLUTIONS AND REAGENTS

It is essential to use high quality, Type 1, 18.2 MΩ-cm deionized water in trace analysis determinations, and it should contain as little dissolved gas as possible. Degas the deionized water using ultrasonic agitation with applied vacuum.

Prepare the Corning 225 mL polystyrene tissue culture flasks two days or more prior to preparing standards and samples. Rinse each flask five times with deionized water, fill it to the top with deionized water, and let it soak overnight. Repeat this daily until flasks are needed for the standards and samples. (See Application Update 142 for additional precautions needed when determining trace ion concentrations.⁵)

Stock Strontium Standard Solution

To prepare a 250 mg/L stock strontium standard solution, dissolve 0.761 g of strontium chloride hexahydrate (FW 266.62 g/mol) with 200 g of 18.2 MΩ-cm deionized water in a pre-cleaned 225 mL tissue culture flask. Gently shake the flask to thoroughly mix the solution.

Primary and Working Strontium Standard Solutions

To prepare a 50 µg/L strontium primary standard, pipette 40 µL of the 250 mg/L stock strontium standard solution into a pre-cleaned 225 mL tissue culture flask. Dilute to 200 g total weight with 18.2 MΩ-cm deionized water. Gently shake the flask to thoroughly mix the solution.

Prepare 10, 20, 50, 100, and 200 ng/L strontium individual working standards similar to the primary standard by pipetting 40, 80, 200, 400, and 800 µL, respectively of the 50 µg/L strontium primary standard solution into separate pre-cleaned 225 mL polystyrene flasks, and diluting to 200 g total weight with 18.2 MΩ-cm deionized water.

Store all standards at 4 °C. Prepare the working and primary standard solutions weekly and the stock standard solution monthly.

Samples

A non-radioactive strontium salt in deionized water was used to develop this application. However, this application is intended for radioactive isotopes and nuclear energy safety protocols must be followed when handling radioactive samples.

SYSTEM PREPARATION AND SETUP

This Application Note describes the proper setup of an ICS-2000 RFIC system, AXP pump, and pressurized sample vessel.

Configuring the System

The AXP Pump is interfaced to the ICS-2000 system through the computer. Connect the RS232 cable to the back of the AXP Pump and the other end of the cable with one of the RJ-11 adapters to the computer. Refer to the AXP Pump manual for more information.⁵

To configure the AXP pump with the ICS-2000 IC system, open the Chromeleon Configuration program, connect to *Chromeleon Server*, select ICS-2000 under *IC: Integrated Systems*, add the ICS-2000 as a device, and select the Module Serial No. on the General Tab. Enter the EGC II MSA cartridge serial number under the ICS-2000 eluent generator tab. To add the AXP pump, select and add AXP Pump located under *IC: Modules*. Under the General tab, Enter AuxPump for the device name to prevent confusion with the ICS-2000 pump. Select AXP Pump under the Device Type tab. Check the configuration under *Server*, then save and close the configuration. A separate instrument panel is needed to control the AXP Pump. Open the Chromeleon program, and select the AXP Pump (Control) Panel on the Browser menu (File Open, Dionex Templates, Panels, Dionex_IC, AXP Pump Panels) to control the pump. Save the AXP Pump Panel under the Timebase or a Sequence. Open a default Control Panel for the ICS-2000 system.

To setup the ICS-2000 RFIC-EG system, install and condition the EluGen EGC II MSA cartridge and a CR-CTC II according to the ICS-2000 Operator's Manual⁷ or the QuickStart instructions received with the consumables. Install the 3 mm IonPac CS12A guard and analytical columns after the injection valve using red PEEK tubing according to the column product manual.⁸ (Refer to the Experimental section for tubing sizes.) Install yellow PEEK tubing before the injection valve to increase the backpressure at 0.5 mL/min to 2200–2500 psi. Do not allow the system backpressure to exceed 3000 psi, as this can damage the degas module. Install the IonPac TCC-XLP1 concentrator column, using black PEEK tubing, in place of the sample loop with the direction of sample loading opposite the direction of analytical flow. The use of concentrator columns is thoroughly discussed in Technical Note 8 (TN8)⁹ and the column manual.¹⁰ Flush the columns with 30 mM MSA for at least 15 min at 0.5 mL/min prior to installing the suppressor.

Hydrate the CSRS 300 suppressor for 20 min according to the QuickStart instructions received with the suppressor. Install the red PEEK tubing backpressure coil in the *Cell Out* port of the cell. Measure the backpressure by measuring the pressure difference from the pump to *Cell In* with and without the backpressure coil. If necessary, adjust the coil length to achieve 30–40 psi backpressure. Install the suppressor and connect the free end of the backpressure coil to the *Regen In* on the suppressor. Equilibrate the columns with 30 mM MSA for at least 1 h at 0.5 mL/min. We recommend equilibrating the column overnight for trace applications. Typically the background conductivity after the initial equilibration is $\sim 0.8 \mu\text{S}$ and stabilizes around $\sim 0.3 \mu\text{S}$ after 24 h.

Use the AXP Pump with the sample vessel container pressurized with 3–5 psi of an inert gas. The AXP pump concentrates a 25 mL sample from the pressurized sample vessel onto the concentrator column. To prepare the AXP pump for trace ion analysis, remove the AXP pump diaphragm according to the instructions in the AXP Pump Manual.⁶ Use nitrile gloves to minimize contamination while working on the pump. Thoroughly rinse the pump parts with 18.2 M Ω -cm deionized water and reassemble the pump without the diaphragm. Install orange PEEK tubing from the pressurized sample vessel to the AXP pump inlet check valve, a yellow PEEK backpressure tubing from the AXP pump outlet check valve, and black PEEK tubing from the free end of the yellow PEEK tubing and into the injection valve (Figure 1). Adjust the backpressure tubing to provide 2500 ± 200 psi on the AXP pump.

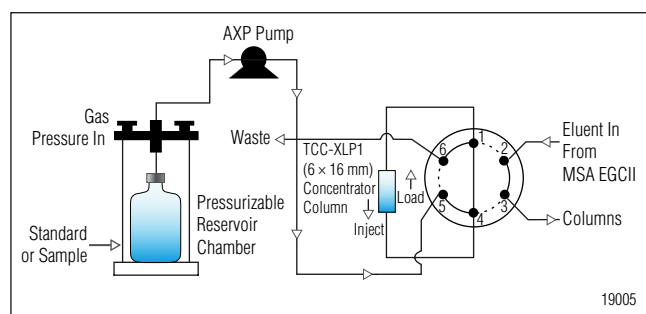


Figure 1. Ion chromatography preconcentration system.

To minimize sample contamination between samples, rinse the outside of the sample tubing and drain the previous sample from the tubing by removing the orange PEEK sample introduction tubing from the pump. To improve priming of the AXP pump, pressurize the sample vessel and allow new sample to flush through the orange PEEK sample introduction tubing for 15 s, and then re-install the sample introduction tubing. Calibrate the AXP pump gravimetrically to a 2.5 mL/min flow rate. Adjust the flow rate setting if necessary and use this setting in the Chromeleon program. Check the flow rate periodically to ensure that the flow rate is stable.

To create an instrument program, enter the parameters in the Conditions section and the pump commands in Table 1. Enter the AXP pump commands manually into the program using Control, Command under AuxPump.

Table 1. AXP Pump Commands for the Instrument Program		
Time (min)	Command	Description
-10.1 ^a	Auxflow = 2.5 ^b Run = 1	Turns on the AXP pump and sets the flow to 2.5 mL/min.
-10.0	Load	Load 25 mL of sample onto the concentrator column.
0	Inject	Elutes the sample from concentrator column onto the guard and analytical columns.
0.2	Run = 0	Turns off the AXP pump.
2.0	Run = 1	Starts overlap, turns on the AXP pump, and starts flushing the sample from the PEEK tubing to waste.
7.0 ^c	End	Ends run.

^aIncrease the starting time to -15.1 min for the first sample in a sequence to flush the sample through the sample lines.

^bEnter the setting used to calibrate the flow rate.

^cCreate a separate stop program at the end of the sequence to turn off the AXP pump.

RESULTS

Radioactive strontium has the same ion-exchange behavior as the stable strontium isotope, and therefore the isotopes elute as a single peak. In published carrier-trace methods, the non-radioactive strontium carrier was added at 10 orders of magnitude higher concentration than ⁹⁰Sr to facilitate a measurable strontium peak.^{2,3} The combined peak is collected by fraction collection and tested by liquid scintillation counting. One author reported an estimated detection limit of 1 Bq/L³, when using a 10 ppm carrier.

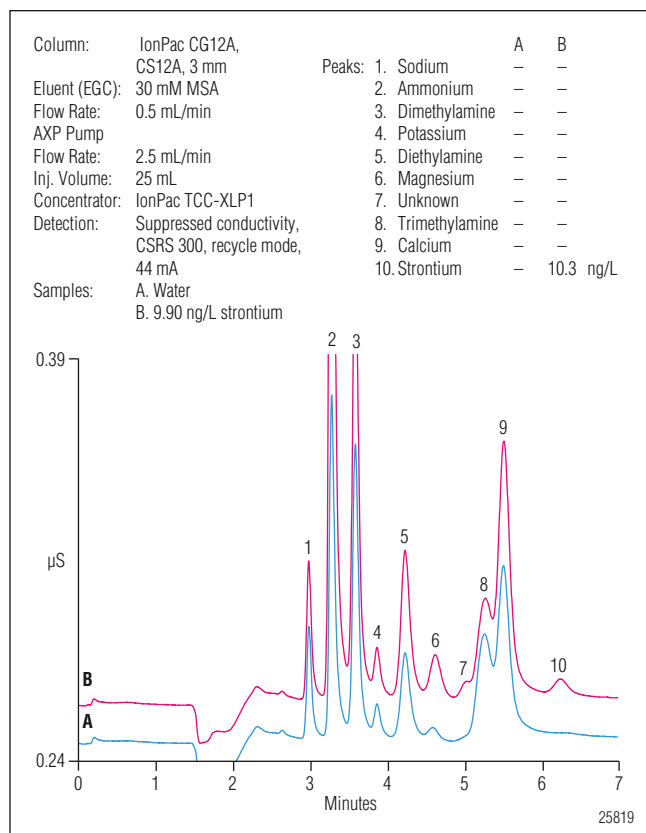


Figure 2. Comparison of A) water and B) 10 ng/L strontium.

In this application, non-radioactive strontium from a 25 mL preconcentrated sample was resolved from calcium, other common inorganic cations, and alkylamines on an IonPac CS12A-5 μm column using 30 mM MSA at 0.5 mL/min (Figure 2B). The IonPac CS12A-5 μm column was selected because it is optimized for fast separations of common cations. To determine the optimum eluent concentration with the shortest run time, the resolution between strontium and calcium at MSA concentrations of 20–35 mM was compared to run time. The experiments showed that strontium was fully resolved ($R_s = 3.6$ (EP)) from calcium with a 7 min run time using 30 mM MSA eluent.

In pre-concentration methods, high ionic strength samples or concentrating too much sample can cause saturation of the concentrator column resulting in poor chromatography and analyte recovery. To determine whether the sample injections were overloading the concentrator column, we measured the peak response of duplicate injections of 10 and 25 mL of 25 ng/L strontium in deionized water concentrated at 1 mL/min. The peak areas of the 10 and 25 mL samples averaged 0.61 and

1.56 $\mu\text{S}\cdot\text{min}$. As expected for samples prepared in deionized water, the peak areas were proportional to the sample volume ($\sim 2.6\times$), confirming that the 25 mL samples are not overloading the IonPac TCC-XLP1 concentrator column. Column breakthrough determinations are thoroughly discussed in TN8.⁹

To reduce the sample preparation time, we evaluated the peak height of 25 mL concentrated volume of 1 ng/L strontium using AXP flow rates from 1.0 to 5.0 mL/min at 0.5 mL/min increments. A backpressure loop appropriate for each flow rate was installed and the AXP pump was calibrated at each flow rate. The peak height was compared with the gravimetrically determined flow rate for each injection. The experiments showed that there was no decrease in peak height with sample load rate. However, the results also showed that strontium peak areas had larger standard deviations at flow rates from 3 to 5 mL/min than at flow rates from 1 to 2.5 mL/min. The measured flow rate programmed for 2.5 mL/min was 2.58 ± 0.01 mL/min (0.2% RSD) with peak area of 0.210 ± 0.001 $\mu\text{S}\cdot\text{min}$ (0.3% RSD) whereas the measured flow rate for 5.0 mL/min was 5.04 ± 0.01 mL/min (0.1% RSD) with a peak area of 0.223 ± 0.003 $\mu\text{S}\cdot\text{min}$ (1.5% RSD). Therefore, a sample load rate of 2.5 mL/min was selected as the compromise between sample preparation time and precision in sample concentration.

Method Qualification

To qualify the method, we determined the linearity, estimated limit of detection (LOD), and the peak area precision for replicate injections of a standard. To determine the LOD, the peak to peak noise was determined per min in three 60 min runs of deionized water, which produced an average noise of 0.25 nS. Figure 2A shows a representative deionized water injection. The calculated LOD was 2.3 ng/L ($S/N = 3$). The linearity of strontium was determined by calibrating with triplicate injections of five standards from 10 to 200 ng/L strontium and comparing the peak area responses to concentration ($r^2 = 0.9992$). To determine peak area precision, 18 injections each of three preparations of 25 ng/L strontium were injected over four days. The 25 ng/L strontium standards averaged 25.22 ± 0.33 ng/L (1.33% RSD) (Figure 3).

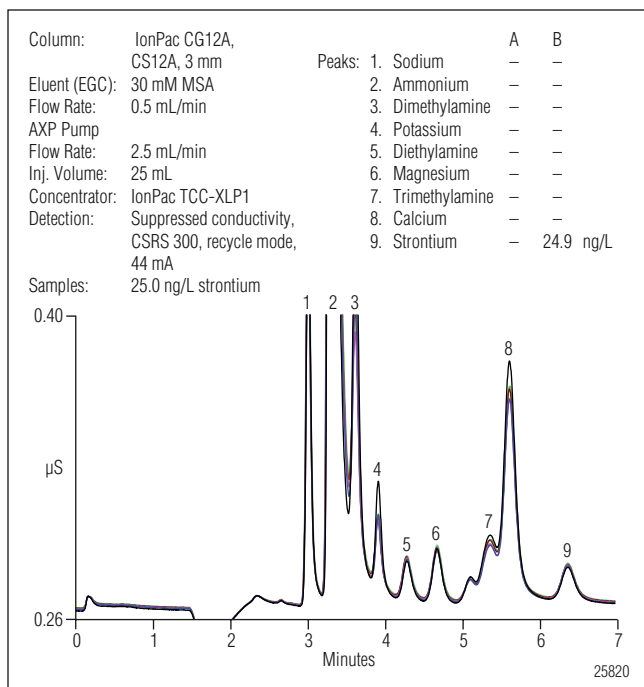


Figure 3: Comparison of six replicate injections of 25 ng/L strontium.

CONCLUSION

This Application Note demonstrates sensitive and accurate determinations of ng/L concentrations of non-radioactive strontium in deionized water using pre-concentration of a 25 mL sample with an RFIC-EG system. This method enables the detection of 8 ng/L of non-radioactive strontium. The application is intended as a separation method for concentrating and isolating ⁹⁰Sr using stable strontium as the carrier. Strontium-90 can be collected using a fraction collector for liquid scintillation counting quantification. This method should be effective for concentrating and isolating radioactive and stable strontium and is applicable to other radioactive cations.

PRECAUTIONS

Take precautions to reduce cross contamination when analyzing trace concentrations of ions. Rinse and drain the sample tubing between samples, pre-clean sample containers, and follow other recommendations for trace ion analysis as described in AU142.⁵ The AXP pump controls the amount of sample loaded onto the concentrator, therefore it is critical to calibrate and periodically verify the AXP pump flow rate.

Determine the breakthrough volume of the concentrator column when concentrating high ionic strength samples or samples >25 mL to ensure the sample is not overloading the concentrator column and the analyte is fully recovered. The peak area response should be proportional to concentration and the amount injected.

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