Sequential Injection Analysis System Exploiting On-line Solid-phase Extraction for the Determination of Strontium and Nickel by Microwave Plasma Atomic Emission Spectrometry

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A sequential flow-based analysis system with on-line solid-phase extraction (SPE) columns coupled to microwave plasma atomic emission spectrometry (MP-AES) was developed for strontium and nickel determination. Crown ether chromatographic resin and dimethylglyoxime polymethacrylate resin were used for strontium and nickel retention under acidic and basic conditions, respectively; eluted with a nitric acid solution in both cases followed by MP-AES detection. The calculated detection limits were 0.25 μg L⁻¹ for strontium and 3.56 μg L⁻¹ for nickel.

Keywords Sequential injection technique, solid-phase extraction, strontium, nickel, atomic emission spectrometry

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Introduction

In 2011, radioactive nuclides were released to the environment after an accident at Fukushima Daiichi Nuclear Power Plant, such as beta emitters, like strontium-90 and nickel-63 with half-lives of 28.7 and 100.1 years, respectively.¹⁻³ These radioisotopes behave in a similar way as in their stable states, representing a threat to human health.⁴⁻⁵ The common radiochemical separation techniques for selective measurements of radioisotopes that employ methods for strontium and/or nickel determination in environmental samples are laborious, time consuming and expensive.⁶ Thus, a fast detection methodology with affordable cost is needed for measuring stable strontium and nickel that could be incorporated to the radiometric analysis of environmental samples.

Recently, solid-phase extraction (SPE) has widely been employed for the analysis of different analytes of relevance in environmental issues where high selectivity and sensitivity are required.¹⁻¹¹ Meanwhile, several SPE methods have been proposed for radiochemical separation using stable strontium and stable nickel as carriers for determining their radioactive isotopes in environmental samples. These radiochemical separation techniques are usually followed by radiation counting (e.g. liquid scintillation counter (LSC)) and/or isotopic analysis (e.g. inductively coupled plasma mass spectrometry (ICP-MS)). Disregarding the reported high sensitivity of the earlier referred methods, their implementation involved many steps and/or high concentration of the reagents utilized. This could represent a drawback when continuous analyses of a big number of samples and/or multiparametric determination are required.¹,²,⁶,¹²⁻¹⁶

The aim of this work is to develop a selective, speedy and economic methodology using solid-phase extraction for the sequential determination of strontium and nickel by microwave plasma atomic emission spectrometry, as an alternative multielement technique for possible application to measure the recovery efficiencies of their stable isotopes usually employed at high concentrations in radiometric analysis of environmental water samples.

Experimental

Apparatus and procedure

The proposed flow-based analysis system is shown in Fig. 1. The system consisted of a syringe pump (25 mL of volume) with a solenoid valve atop (SPV, Gilson, USA), an 8-port selection valve (SV, Hamilton, USA) and two 6-port switching valves (SWV1, SWV2, Hamilton, USA) with respective on-line SPE columns connected to each one; it is computer controlled by a home-made software for performing the instruction sequence shown in Table S1 in Supporting Information. The manifold was built of PTFE tubes with an inner diameter of 0.5 mm, except for the holding coil, which had an inner diameter of 1.59 mm (15 mL of volume). The atomic emissions of strontium and nickel were measured at wavelengths of 407.771 and 352.454 nm, respectively. The MP-AES settings are shown in Supporting Information.

Reagents

All the solutions used in this work were prepared using analytical-grade reagents with deionized water. Standard solutions of stable strontium and stable nickel were prepared by the proper dilution of stock standard solutions with 10% HNO₃ and 0.2 mol L⁻¹ ammonium citrate (pH = 8 - 9) prior to use, respectively. A 10% HNO₃ solution was employed for Sr resin conditioning and a 0.2 mol L⁻¹ ammonium citrate solution (pH set between 8 - 9 with ammonia solution) was utilized for Ni resin conditioning. The eluent solution employed in the
determination of both analytes was 1% HNO₃. The details of the reagents employed are displayed in Supporting Information.

**Extraction columns**

The Sr resin (Eichrom, USA) extractant is composed of 4,4′-di-t-butylcyclohexano 18-crown-6 (crown ether) for strontium retention through the formation of nitrate complexes under acidic conditions. Meanwhile, Ni resin (Eichrom, USA) is based on the dimethylglyoxime (DMG) precipitation chemistry for nickel analysis. Furthermore, a pre-filter resin (Eichrom, USA) is an acrylic ester polymeric resin employed for the removal of organic impurities, in this work, coeluted DMG from the Ni resin. The selectivity of Sr resin and Ni resin represents a great advantage for the radiometric analysis of strontium and nickel in environmental water samples due to their low retention of other elements under given conditions. The preparation of the employed extraction columns is shown in Supporting Information.

**Results and Discussion**

**Optimization**

The optimal operations conditions involving the volume of the columns, as well as the amounts of Ni resin and pre-filter resin and their arrangement in the column for enhancing the Ni analytical signal and the removal of leached DMG from Ni resin, were set during the preliminary experiments. A distortion of the baseline at adjacent wavelengths to the analyte wavelength signal was observed because of the higher ratio of the Ni-DMG complex reaching the plasma; this was taken in consideration for further experiments. A comparison of the analytical peak signals obtained using and without using a pre-filter resin is shown in Fig. S1 in Supporting Information. Two columns with a volume of 0.4 mL, one column with Sr resin only for the strontium preconcentration and another for nickel extraction containing 0.2 mL of Ni Resin and 0.2 mL pre-filter resin were prepared. The volume of the columns used in this work drastically reduced the consumption of resins compared to the 2 mL columns employed in batch-wise methods. The concentration of the eluent solution, 1% HNO₃, was adopted following the specifications given by the manufacturer (Agilent Technologies) of the MP-AES.

Using respective standard solutions of 100 µg L⁻¹ Sr in 10% HNO₃ and 1000 µg L⁻¹ Ni in 0.2 mol L⁻¹ ammonium citrate (pH = 8 – 9), the optimal conditions to produce the best possible analytical response were determined by the univariate method. The concentration ranges of 1 to 50% HNO₃ and 0.01 to 0.2 mol L⁻¹ ammonium citrate were studied, obtaining the optimal value of 10% HNO₃, thus achieving the usage of a lower concentration for conditioning and rinse of the Sr resin than in those works previously reported. Meanwhile, an optimal value of 0.2 mol L⁻¹ ammonium citrate (pH = 8 – 9) is in agreement with the concentration employed in the batch-wise methods for the nickel preconcentration in Ni resin, but achieving a reduction in its consumption during conditioning and rinsing steps due to the smaller column employed. A volume of 1% HNO₃ eluent solution was analyzed in the range of 0.5 to 5 mL, obtaining that 1 mL of 1% HNO₃ was the optimal for the elution of a sample in both methodologies. Different sample volumes for analyte preconcentration into their respective columns were examined in the range of 1 to 10 mL. The maximum sample volume tested was 10 mL to avoid any sample introduction into the syringe due to the 15 mL limitation of the holding coil. It was observed that a bigger sample volume employed in the preconcentration step for strontium determination corresponded an increase in the analytical signal obtained. Meanwhile, in the nickel methodology a plateau was reached after a 5-mL volume of the sample, indicating saturation of the Ni resin. Although the detection limit was also calculated using 10 mL of the sample; a sample volume of 3 mL was chosen as a compromise between the speed of analysis and the sensitivity of the method for applications to environmental water samples from Fukushima.

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**Fig. 1** Schematic diagram of the proposed system. SPV, syringe pump with a solenoid valve atop; SV, selection valve; SWV₁ and SWV₂ are switching valves with columns; Sr, strontium resin column; Ni, nickel resin and pre-filter resin column; MP-AES, microwave plasma atomic emission spectrometry detector.
Analytical characteristics

A linear calibration graph and analytical signals obtained by the proposed system using 3-mL samples are shown in Fig. 2. The performance of this work was calculated employing stable strontium and stable nickel in ranges of 0 – 200 μg L⁻¹ (slope = 162.04, \( R^2 = 0.9999 \)) and 0 – 2000 μg L⁻¹ (slope = 5.29, \( R^2 = 0.9999 \)), respectively. The limits of detection (3\( \sigma \)) of the proposed method were calculated, obtaining 0.25 μg L⁻¹ for strontium and 3.56 μg L⁻¹ for nickel. In addition, the limits of detection (3\( \sigma \)) of 0.19 μg L⁻¹ Sr and 3.33 μg L⁻¹ Ni using 10 mL of a sample were calculated. The detection limits achieved in this work improved the 10 μg L⁻¹ obtained for stable strontium in the determination of radioactive strontium by Fajardo et al.\(^{12}\) even though the detection limits for nickel are vaster than the instrument detection limits of 20 μg L⁻¹ Ni for environmental samples given by the MP-AES manufacturer; they still are lower than the 2 mg L⁻¹ of stable nickel commonly employed for radiochemical analysis using Ni resin extraction.\(^{16}\) Therefore, the proposed system could be considered to be a possible sample pretreatment method in the radiometric analysis of environmental water samples. The efficiency of the columns for the preconcentration of both analytes was 99% up to 150 analytical cycles with a RSD of 3.2% for strontium and 1.2% for nickel. The frequency of analysis was 5 – 9 samples per hour with an enrichment ratio of 3:1 – 10:1, depending on the sample volume (3 – 10 mL) employed.

Interferences

In environmental samples, Ca²⁺, K⁺ and Mg²⁺ are commonly found at high concentrations in relation to Sr and Ni, consequently considered as possible interferants.\(^{14}\) Furthermore, considering the specifications given by the resin manufacturer (Eichrom), the influence of Ba²⁺ onto Sr resin and Fe³⁺ over Ni resin was examined. The above-mentioned potentially interferent ions were considered in this study following the criteria of which may be retained by the resins and their possible beta-emitter radioactive isotopes existence in those environmental samples which this proposed method could be applied during radiochemical analysis.\(^{12}\) Finally, the co-existence of the analytes was studied. Considering an error of ±5% to be tolerable, the results showed that Ba²⁺ and K⁺ present in concentrations of over 10 mg L⁻¹ and Ca²⁺ from 200 mg L⁻¹ interfered in the determination of 100 μg L⁻¹ of strontium. Mg²⁺ and Ni²⁺ up to 400 and 200 mg L⁻¹ as maximum concentrations tested, no interference was observed using the previously-mentioned strontium concentration. Meanwhile, Ca²⁺, K⁺ and Mg²⁺ did not showed any interference in concentrations tested up to 400 and 200 mg L⁻¹, respectively; however, at a concentration of over 100 mg L⁻¹ of Fe³⁺ interference occurred in the determination of 1000 μg L⁻¹ of nickel. The presence of interferent ions during the application of the proposed method is not expected to be at such levels in environmental water samples from Fukushima.

Determination of strontium and nickel in environmental water samples

The proposed system was applied to the analysis of four underground water samples from Fukushima. The analytical results of strontium and nickel determination by the proposed method were compared with those obtained by GF-AAS, as shown in Table 1. In the analysis of strontium, the results by both methodologies showed no significant differences at a confidence level of 95%. Meanwhile, nickel was not found in any of the samples measured by both detectors. Furthermore,

![Fig. 2](image)

**Table 1** Determination of Sr and Ni in underground water samples from Fukushima

<table>
<thead>
<tr>
<th>Samplea</th>
<th>Quantification value of Sr/μg</th>
<th>Quantification value of Ni/μg</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>The proposed methodb</td>
<td>GF-AASb</td>
</tr>
<tr>
<td></td>
<td>Addedc</td>
<td>Found</td>
</tr>
<tr>
<td>Underground water 1</td>
<td>0.0</td>
<td>17.9 ± 0.8</td>
</tr>
<tr>
<td>100.0</td>
<td>123.4 ± 1.0</td>
<td>105</td>
</tr>
<tr>
<td>Underground water 2</td>
<td>0.0</td>
<td>20.8 ± 0.1</td>
</tr>
<tr>
<td>100.0</td>
<td>120.6 ± 0.8</td>
<td>100</td>
</tr>
<tr>
<td>Underground water 3</td>
<td>0.0</td>
<td>26.1 ± 0.2</td>
</tr>
<tr>
<td>100.0</td>
<td>128.1 ± 0.5</td>
<td>102</td>
</tr>
<tr>
<td>Underground water 4</td>
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<td>N.D.</td>
</tr>
<tr>
<td>100.0</td>
<td>104.2 ± 0.7</td>
<td>105</td>
</tr>
</tbody>
</table>

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a. Underground water 1, 2 and 3 were collected from wells of coast side of Iwaki-city, Fukushima pref., Japan. Underground water 4 was collected from a storage tank of Fukushima Daiichi Nuclear Power Plant that was built to store underground water after pumping from the mountain side (underground water bypass). b. Water samples were diluted 10-fold, three replicates were carried out. c. Water samples were diluted 2-fold, three replicates were carried out. d. Concentration of Sr or Ni spiked into the water samples, respectively. N.D.: Not detected. e. Known concentration of Sr or Ni was not spiked into water samples for measuring by GF-AAS.
we contemplated the concentrations of stable strontium and stable nickel usually employed in the radiometric analysis of environmental water samples; respective concentrations of 100 μg L⁻¹ of strontium and 1000 μg L⁻¹ of nickel were spiked into samples for testing the accuracy of the proposed method. The recovery percentages of the known spiked concentrations were calculated by subtracting the original concentration of the analyte to the value obtained of a spiked concentration plus the original concentration; the resulting value was divided by the spiked concentration and the obtained ratio times by 100. The recovery percentage values of the spiked concentrations were within 100 - 105% for strontium and within 99 - 102% in the case of nickel; a value of 100 ± 5% was considered acceptable.

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Supporting Information

This material is available free of charge on the Web at http://www.jsac.or.jp/analsci/.

References