

1 **Novel approach for strontium preconcentration from seawater and**
2 **rapid determination of ^{89,90}Sr in emergency situations**

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12
13 **Highlights**

- 14 • Novel approach for rapid determination of Sr radionuclides in seawater is proposed
- 15 • Synthetic zeolite 4A was used for preconcentration of Sr and then dissolved in HNO₃
- 16 • Automated Sr separation was conducted on SuperLig[®]620 column
- 17 • Sr separation from 1 L of seawater takes 1.5 h with recoveries of 89 ± 4%
- 18 • MDA were 0.74 Bq/L for ⁸⁹Sr, and 1.47 Bq/L for ⁹⁰Sr, at their ~ 10:1 activity ratio

19
20 **Abstract**

21 A novel approach for rapid ^{89,90}Sr determination in seawater samples is developed. For the first
22 time in the radioanalytical application, the features of the synthetic zeolite Z4A and a highly
23 selective material for Sr separation were synergically employed. Seawater composition
24 significantly reduces Sr yield on highly selective solid-phase extraction materials, making the

25 preconcentration step essentially important but laborious and time-consuming. To address this
26 issue, the ability of zeolite 4A to concentrate the Sr from the seawater matrix was employed. With
27 the proposed method, two important goals were achieved: (i) simple preconcentration of Sr that
28 can be conducted directly at the sampling site, enabling a rapid procedure for $^{89,90}\text{Sr}$ determination
29 in emergencies, and (ii) high and stable Sr recoveries ($89 \pm 4\%$) necessary for lowering detection
30 limits. Strontium is effectively separated from 1 L of seawater in less than 1.5 h, which is especially
31 important in emergency situations, such as the Fukushima Daiichi Nuclear Power Plant accident.
32 Minimum detectable activities achieved for ^{89}Sr : ^{90}Sr activity ratio $\sim 10:1$ were 0.74 Bq/L for ^{89}Sr ,
33 and 1.47 Bq/L for ^{90}Sr , detected by Cherenkov counting, 36 to 38 h after separation, and 30 min
34 counting time.

35

36 **Keywords:** $^{89,90}\text{Sr}$, Seawater, Zeolite Z4A, Preconcentration, Rapid determination, Emergency.

37

38 **Introduction**

39

40 After the Fukushima Daiichi Nuclear Power Plant (FDNPP) accident, numerous reports and
41 scientific papers were focused on radioactive cesium spreading in Fukushima's surroundings and
42 globally, while only a limited number of studies have considered the environmental behavior of
43 released radioactive strontium [1]. Seawater was initially pumped into the reactors to maintain
44 cooling during the emergency [2], and the majority of ^{90}Sr was discharged as cooling water to the
45 Pacific Ocean [3]. The initial releases of radioactive strontium were not expected to be as high as
46 for other radionuclides during the accident, however, an additional key reason for less extensive
47 research on the spread of $^{89,90}\text{Sr}$ lies in the methodology for their quantitative determination. While

48 cesium isotopes can be directly determined by gamma-ray spectrometry, the determination of
49 radioactive isotopes of strontium implies the use of complicated and time-consuming separation
50 methods before detection and quantification [2–4]. Chemically similar to calcium, ^{90}Sr is easily
51 incorporated in bone tissue, emitting highly energetic β particles, mainly during the decay of its
52 short-lived daughter ^{90}Y , increasing the chance of leukemia or bone cancer. Determining activities
53 of ^{90}Sr is mandatory in many environmental monitoring programs, including the monitoring of
54 leakage of this contaminant from FDNPP reactors and storage tanks to the ocean. Therefore,
55 developing rapid and simple radiochemical procedures for radiostrontium determination is
56 imperative to avoid the drawbacks of existing methodologies.

57 The complexity of seawater (SW) composition, especially a high concentration of several
58 cations (~ 10000 mg/L of Na, 1200 mg/L of Mg, 400 mg/L of Ca, and 400 mg/L of K) with respect
59 to the mean total Sr concentration of 8.0 mg/L [5], impede Sr separation and determination [6].
60 The standard procedure for radiostrontium determination includes the preconcentration step,
61 separation of pure Sr from bulk, yttrium separation after secular equilibrium between ^{90}Sr - ^{90}Y , and
62 subsequent detection of ^{90}Y and $^{89,90}\text{Sr}$. Mostly all developed radiostrontium determination
63 methods follow this sequence with the difference in preconcentration and/or separation methods
64 for pure strontium isolation.

65 In recently published papers, various methods were developed by using materials for solid-
66 phase extraction, Sr resin ($^{89,90}\text{Sr}$), DGA resin (^{90}Y), or Sr Rad Disk [7–11]. However, to increase
67 yields of the methods, most of the interfering cations must be previously removed because SW
68 substantially reduces strontium yield on highly selective solid-phase extraction materials such as
69 Sr resin and/or SuperLig[®] 620 (material also used in Sr Rad Disks). By mixing 1 L of SW with
70 concentrated HNO_3 to 3 mol/L and directly loading on the Sr resin (3 g), 50% of Sr recovery can

71 be maximally achieved, depending on the size of Sr resin particles [12]. On the other hand, the
72 SuperLig[®]620 column does not bind Sr from SW [13].

73 Consequently, for Sr determination in SW, mostly phosphates [7,8], carbonates [10,11,14], or
74 oxalates [15] were primarily used as agents for preconcentration and partial removal of other
75 cations. It should be noted that a preconcentration step is necessary for the determination of
76 radioactive strontium in SW (i.e., seas and oceans) to provide an activity level for reliable
77 quantification since its activity is very low due to high dilution even in accidental situations. The
78 preconcentration with these agents usually requires consuming a substantial amount of
79 precipitation agent and strict pH control, which slows down the whole process and results in more
80 waste, especially if larger volumes of samples are used. Therefore, different materials were
81 investigated for simpler and more efficient concentrating of Sr from high saline waters, including
82 zeolites [16].

83 Zeolites' crystalline and highly porous structures provide large surface areas on which cation
84 exchange and chemical reactions take place. Due to high sorption capacity, and resistance to
85 radiation damage [17], zeolites are often used in liquid waste treatment [18,19], soil
86 decontamination, and remediation, for example, after Chernobyl or Fukushima accident [20].
87 Synthetic zeolite 4A exhibits exceptionally high Sr ions capacity compared to other investigated
88 natural and synthetic zeolites [19,21–25]. In our previous work, it was found that the selectivity of
89 zeolite Z4A towards metal ions decreases in an equimolar mixture in the following order: Sr > Ca
90 > K > Mg > Na, therefore, it can extract Sr efficiently even from a complex matrix [24]. From SW,
91 84% Sr, 45 % Ca, 14% K, and 12% Mg were sorbed relative to their initial concentrations at the
92 zeolite 4A dose of 5 g/L.

93 Although zeolite 4A has been broadly tested as a decontamination agent, to the best of the
94 authors' knowledge, the prospects for its radioanalytical application have not been previously
95 considered,, particularly for Sr preconcentration from SW. Accordingly, this study was conceived
96 with the idea of using the selectivity of zeolite 4A to efficiently preconcentrate Sr, reduce the
97 concentration of other cations from SW, and then transfer Sr entrapped in zeolite 4A into a liquid
98 phase from which Sr can be completely separated on highly selective resins. The main objective
99 was to develop and validate a novel method for determining $^{89,90}\text{Sr}$ activities in SW, which is faster
100 and easier to perform than existing ones while providing similar or even better Sr recoveries. The
101 commercial zeolite 4A product intended for water softening in environmentally friendly detergents
102 was used in the study as a cost-effective and available material. The overall method involves
103 enrichment of Sr from 1 L of SW by zeolite Z4A with high yield, dissolution of zeolite Z4A with
104 the nitric acid, automated Sr separation on a 1 mL SuperLig®620 column, and quantitative
105 simultaneous determination of ^{89}Sr and ^{90}Sr .

106

107 **Materials and methods**

108

109 **Zeolite 4A**

110 Synthetic zeolite (denoted Z4A) was supplied by the Zvornik Alumina Refinery (Bosnia and
111 Herzegovina), which uses the Bayer process liquids for zeolite synthesis. The Z4A is a crystalline
112 product containing 36% Al_2O_3 , 22% Na_2O , 42% SiO_2 (the Si/Al ratio is 1.06), with cubic particles
113 of uniform size ($\sim 4\ \mu\text{m}$), a pore diameter of 4 Å, and the alkaline reaction in water (pH value of
114 the 10% suspension is 11.2) [24]. The material was used without further treatments.

115

116 Sorption of Sr from seawater matrix by Z4A

117 To provide efficient sorption of Sr ions from the seawater matrix by Z4A, the effects of the
118 contact time and the dose of Z4A were firstly investigated in batch conditions using synthetic
119 seawater (SSW). SSW was prepared by dissolving 36.0 g of the aquarium salt mix (Coral pro salt
120 mix - Red Sea) in 1 L of deionized water. The SSW contained 10500 mg/L Na⁺, 440 mg/L Ca²⁺,
121 400 mg/L K⁺, 1310 mg/L Mg²⁺, 8.25 mg/L Sr²⁺, 2700 mg/L SO₄²⁻, 19450 mg/L Cl⁻, 56 mg/L Br⁻,
122 142 mg/L, CO₃²⁻/HCO₃⁻, 0.06 mg/L I⁻, and the pH of the solution was 8.3. The sorption
123 experiments were performed at room temperature (21±1 °C) by varying Z4A to SSW ratio in the
124 range of 2 g/L – 30 g/L (0.040-0.600 g Z4A in 20 mL), and the contact time between 5 min and
125 6 h. Separate batches were prepared for each solid-to-solution ratio and contact time and mixed
126 using the overhead laboratory shaker (Heidolph™ Reax) at 10 rpm. After membrane filtration
127 (0.45 µm pore size), the residual Sr concentrations were measured by Inductively Coupled Plasma
128 Optical Emission Spectrometer (ISP-OES) Avio 200 (Perkin Elmer). The calibration standards for
129 the determination of Sr concentration in SW were prepared in the artificial seawater solution
130 (10000 mg/L Na, 1250 mg/L Mg, 400 mg/L Ca, and 400 mg/L K) [26]. The experiments were
131 performed in duplicate for each experimental setup, and the results are presented as mean values.
132 The morphology of Z4A particles before and after interaction with SSW at optimized conditions
133 was compared using JEOL thermal field emission scanning electron microscope (FE-SEM, model
134 JSM-7000F).

135

136 Desorption of Sr from Z4A

137 The prospects of Sr recovery from Z4A were tested by batch desorption experiments. Samples
138 were firstly prepared by mixing Z4A with SSW in 50 mL centrifuge tubes at previously optimized

139 conditions (0.200 g Z4A in 20 mL SSW (10 g/L), 10 min of contact), centrifugation (relative
140 centrifugal force (RCF) of 8867×g for 10 min), and filtering the liquid phase through 0.45 μm
141 membrane filters. The Sr concentration in the liquid phases was determined for calculating the
142 amount of Sr sorbed by Z4A. Subsequently, 20 mL of the desorbing solutions containing either
143 NaCl or CaCl₂ at various concentrations (0.1 mol/L, 0.5 mol/L, and 1 mol/L) were mixed with the
144 solid residues and shaken for either 1 h or 24 h, at 10 rpm. All experiments were performed in
145 duplicate. The desorbed amounts of Sr were measured in the filtrates by ICP-OES using the
146 appropriate desorbing solution both as a blank and as a matrix to prepare the calibration standards,
147 and the desorption efficiencies were calculated.

148

149 **Z4A dissolution experiments**

150 The dissolution of Z4A under acidic conditions was tested by mixing 10 g of Z4A with 100
151 mL of solutions having different HNO₃ concentrations, namely 2 mol/L, 3 mol/L, and 5 mol/L.
152 The time required for Z4A to dissolve completely was monitored, and the time after which the gel
153 is formed. Based on the first results, the volume of 2 mol/L was increased to achieve both a high
154 dissolution rate and delayed gelatinization of the sample.

155

156 **Separation of Sr using SuperLig[®]620**

157 SuperLig[®]620 (35-75 μm) was supplied by IBC Advanced Technologies, Inc. (USA). The
158 binding capacity of the resin was provided in the manufacturer Certificate of the Analysis
159 (0.23 mmol Sr/g). The resin was filled in 1 mL columns provided by Supelco (Merck, Germany).

160 The automated separation system was used for column separation. The eight-roller, one-
161 channel Cavro Smart Peristaltic Pump was used for continuous flow applications. Tecan Cavro
162 valves 1 x 4 - port Teflon valve with 1/4-28 fittings were used for sequential injection of the
163 solutions. The in-house software was developed for computer control of the time of the sequence
164 and flow direction.

165 Separation of Sr on SuperLig[®]620 was done as it was described in earlier papers [13,27], with
166 slight modifications. After contact with SSW, Z4A with sorbed Sr was dissolved in 2 mol/L HNO₃,
167 and the solution was automatically loaded onto the SuperLig column ($V = 1$ mL), which was
168 preconditioned with 20 mL of 2 mol/L HNO₃ solution, at a flow rate of 3 mL/min. The column
169 was additionally washed with 20 mL of 2 mol/L HNO₃ solution. Since in emergency case samples,
170 ¹⁴⁰Ba might be present in the samples, the column was washed with 3 mL of H₂O, and Sr was
171 stripped from the column with 20 mL of 0.5 mol/L EDTA solution, pH ~ 6 (flow rate 1 mL/min)
172 directly into a scintillation vial. Samples were repeatedly counted by Cherenkov counting on LSC
173 for 30 to 60 min. In the case of ^{89,90}Sr determination, the activity of ⁸⁹Sr is determined from first
174 counting, while ⁹⁰Sr is determined via ⁹⁰Y ingrowth [28]. The detection limits were calculated
175 according to ISO 11 929 [29].

176

177 **Sample preparation for validation experiments**

178 The efficiency of radiostrontium removal from SSW by Z4A was verified, and the selectivity
179 of Z4A in respect to several other radionuclides was assessed after spiking SW. The natural SW
180 sample was taken from the Adriatic Sea, at location Martinska (7.5 mg/L of Sr) near Šibenik,
181 Croatia. SW samples were spiked with a standard gamma mix (²⁴¹Am, ⁶⁰Co, ¹³⁷Cs), and standard
182 solutions of ⁸⁵Sr, ⁸⁹Sr, ⁹⁰Sr/⁹⁰Y, ⁸⁸Y, ¹³³Ba and/or ²¹⁰Pb, and counted on a gamma counter and on a

183 liquid scintillation counter. Test solutions with radioactive standards were prepared by spiking
184 SSW or natural SW with certified reference solutions of ^{85}Sr ($0.9941 \cdot 10^6$ Bq/g, relative uncertainty
185 1.2 %), ^{89}Sr ($0.9940 \cdot 10^6$ Bq/g, relative uncertainty 1.0 %), $^{90}\text{Sr}/^{90}\text{Y}$ ($1.015 \cdot 10^6$ Bq/g, relative
186 uncertainty 1.0 %), ^{88}Y ($0.9581 \cdot 10^6$ Bq/g, relative uncertainty 1.0 %), ^{210}Pb ($1.01 \cdot 10^6$ Bq/g,
187 relative uncertainty 1.1 %), all ref. date September 18, 2015. and standard gamma mix (^{241}Am ,
188 $3.489 \cdot 10^3$ Bq/g, relative uncertainty 0.3 %, ^{60}Co , $2.222 \cdot 10^3$ Bq/g, relative uncertainty 0.3 %, ^{137}Cs ,
189 $2.003 \cdot 10^3$ Bq/g, relative uncertainty 0.8 %, ref. date August 10, 2015.) which were provided by
190 Czech Metrology Institute (Prague, CZ). Since ^{140}Ba has a short half-life and is not a readily
191 available reference sample, a standard solution of ^{133}Ba ($9.884 \cdot 10^3$ Bq/g, relative uncertainty
192 1.8 %, ref. date September 21, 2010), provided by Analytics (Atlanta, USA), was used instead. All
193 other chemicals were of analytical grade.

194 The prepared test solutions were mixed with Z4A at the doses of 10 g/L for 10 min and
195 filtrated. The filtrate was counted again to determine the recovery of tested radionuclides. Further
196 Sr separation was accomplished as described in the previous section.

197 The recovery of each radionuclide was determined. Detection of ^{89}Sr , $^{90}\text{Sr}/^{90}\text{Y}$ was carried out
198 by Cherenkov counting on the Liquid scintillation spectrometer Tri-Carb 3180 TR/SL in low-level
199 counting mode [13,28]. The counting efficiency of ^{89}Sr in EDTA solution is 32.51 %, while for
200 ^{90}Y 50.05 %. Canberra's characterized Broad energy germanium detector (BEGe; resolution: 1.95
201 keV at 1332 keV, relative efficiency: 48%) with the original lead shielding was used to determine
202 activity concentrations of gamma emitters. Spectra were analyzed by Genie 2000 software, and
203 mathematical calibrations were done with LabSOCS.

204 The applicability of the method was tested by spiking SW with known activity of $^{89,90}\text{Sr}$ or
205 with a proficiency test sample provided by Analytics (Eckert and Ziegler, USA). In the latter case,

206 the aliquot of 1 mL was diluted with 1 L of SW prior to separation. An additional test for ^{90}Sr
207 determination by the proposed method was performed using 1 L of SW proficiency test samples
208 IAEA-RML-2017-01 and IAEA-RML-2021-01 (IAEA, Monaco).

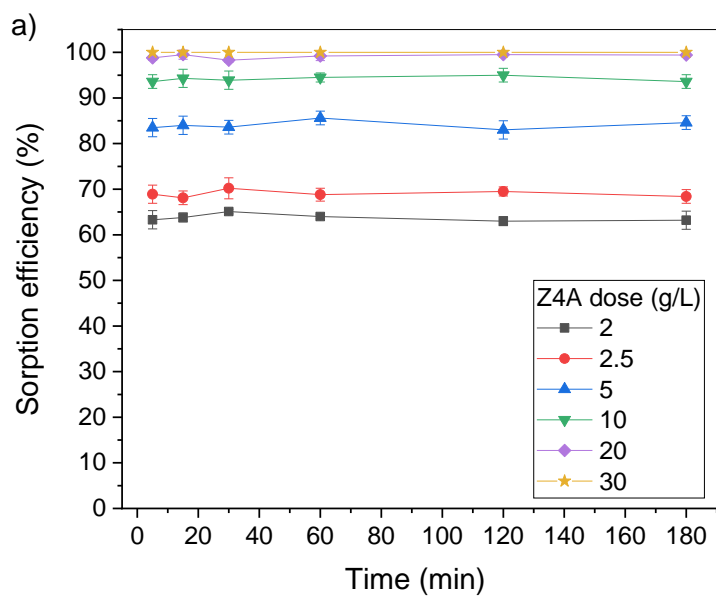
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210 **Results and Discussion**

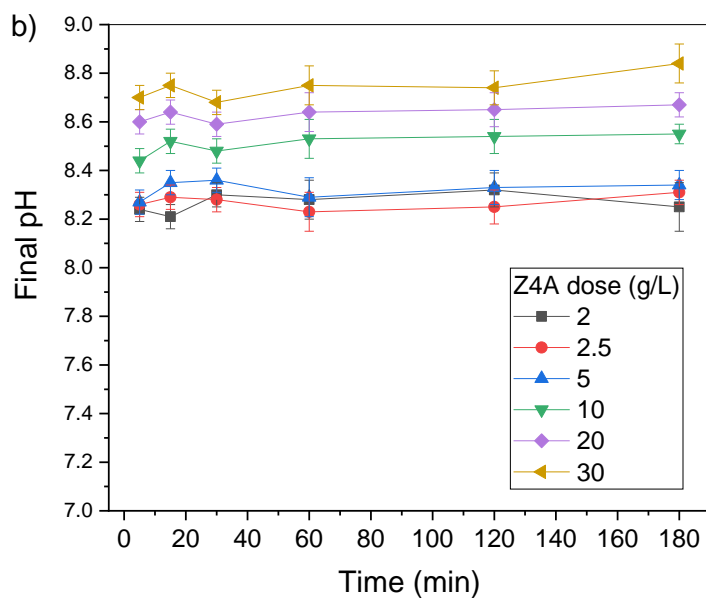
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212 **Optimization of Z4A dose and contact time for Sr preconcentration from seawater matrix**

213 The effect of contact time on Sr sorption efficiency from SSW is displayed in Fig. 1, a, for
214 different doses of Z4A. The efficiency of Sr removal was weakly affected by the increase in
215 equilibration time from 5 min to 6 h, indicating that the process of Sr separation was very rapid at
216 all investigated solid-to-solution ratios. On the other hand, the increase in the Z4A dose from 2
217 g/L to 30 g/L significantly enhanced Sr separation efficiency from $64 \pm 2\%$ to 100%.



218



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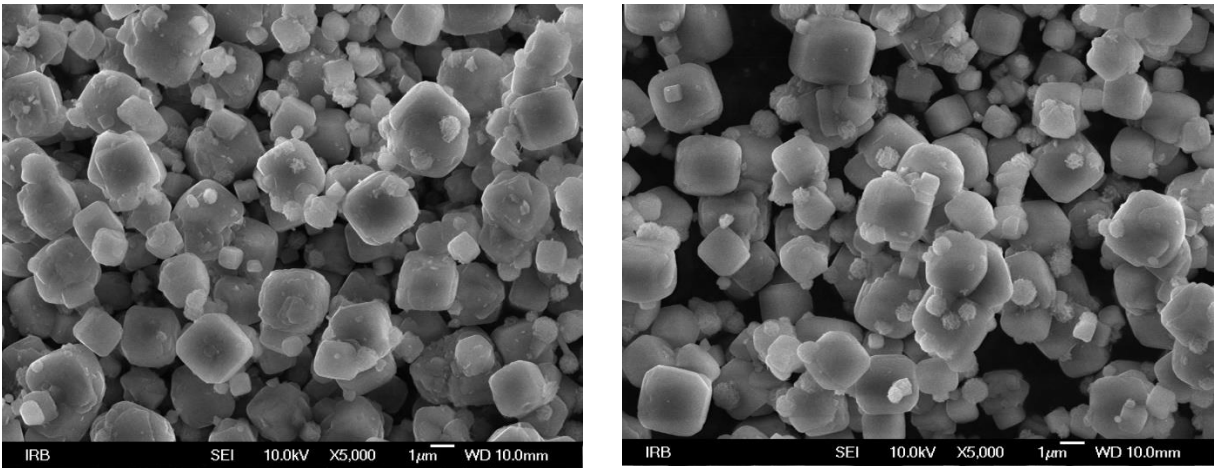
220 **Fig. 1.** The effect of contact time and Z4A dose on: a) Sr sorption efficiency from synthetic
 221 seawater (SSW), b) final pH values. Shaking speed 10 rpm.

222

223 The sorption efficiency of $94 \pm 3\%$ was achieved by mixing 1 g of Z4A with 100 mL of SSW
224 (10 g/L dose), while the doubled amount of Z4A was necessary for an efficiency of $99 \pm 0.5\%$.
225 Therefore, 10 g/L dose has been considered optimal for radioanalytical purposes. For comparison,
226 the yields achieved by precipitation of carbonates were around 80% [12]. However, high amounts
227 of Mg coprecipitate with Sr and Ca, complicating isolation on highly selective Sr materials.
228 Although the co-removal of Mg can be avoided if Sr is precipitated in the form of oxalate, Sr's
229 yields are significantly lower [15].

230 The final pH of SSW was minorly affected by the variation of contact time, while the slight
231 shift from ~ 8.3 to ~ 8.7 was evident with the increase in Z4A dose (Fig. 1, b). These data correspond
232 well with the higher alkalinity of Z4A in respect to SSW. At a Z4A dose of 10 g/L, the pH of SW
233 was ~ 8.4 , matching closely the global average pH value of surface oceans of 8.2, which can
234 fluctuate by ± 0.3 units owing to local, regional, and seasonal factors [30]. Overall results indicate
235 that the Sr can be concentrated almost 100 times directly at the sampling site without pH
236 adjustments, meaningfully speeding up and simplifying the preconcentration process compared to
237 other techniques such as precipitation [17,18,20-22].

238 SEM analysis of the Z4A sample (Fig. 2, a) shows well-defined cubic crystals characteristic
239 for highly crystalline zeolite 4A that remain preserved after contact with SSW at optimized
240 conditions (Fig. 2, b).



(a)

(b)

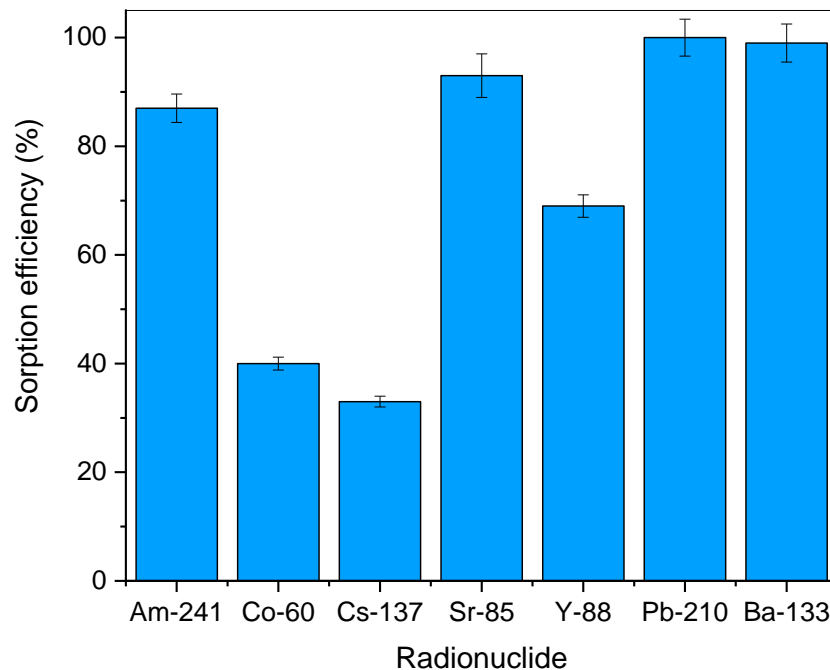
241 **Fig. 2.** SEM images of Z4A particles: a) before and b) after reaction with SSW (Z4A dose 10
 242 g/L, contact time 10 min, shaking speed 10 rpm).

243

244 **Separation of radioactive Sr and other radionuclides from SW**

245 Along with the sorption of radioactive ^{85}Sr , the separation of several other radionuclides from
 246 SW by Z4A was tested at conditions set previously (Fig. 3). Isotopes of $^{134,137}\text{Cs}$, $^{58,60}\text{Co}$, and even
 247 ^{241}Am are the nuclides often present in discharges from NPPs, and along with ^{140}Ba may appear in
 248 the fresh release after an accident, while Pb isotopes are members of natural decay chains.

249 The sorption efficiency of ^{85}Sr in the natural seawater sample was $93 \pm 4.0\%$ at a Z4A dose
 250 of 10 g/L, which corresponds well with the results obtained using stable Sr and SSW (Fig. 1, a).
 251 The Z4A simultaneously removed all investigated radionuclides but with different efficiencies
 252 (Fig. 3). The high-efficiency separation of Am, Pb, and Ba ($87 \pm 2.6\%$, $100 \pm 3.4\%$, $99 \pm 3.5\%$,
 253 respectively) suggests that Z4A as well deserves further investigation regarding their
 254 separation/preconcentration from seawater.



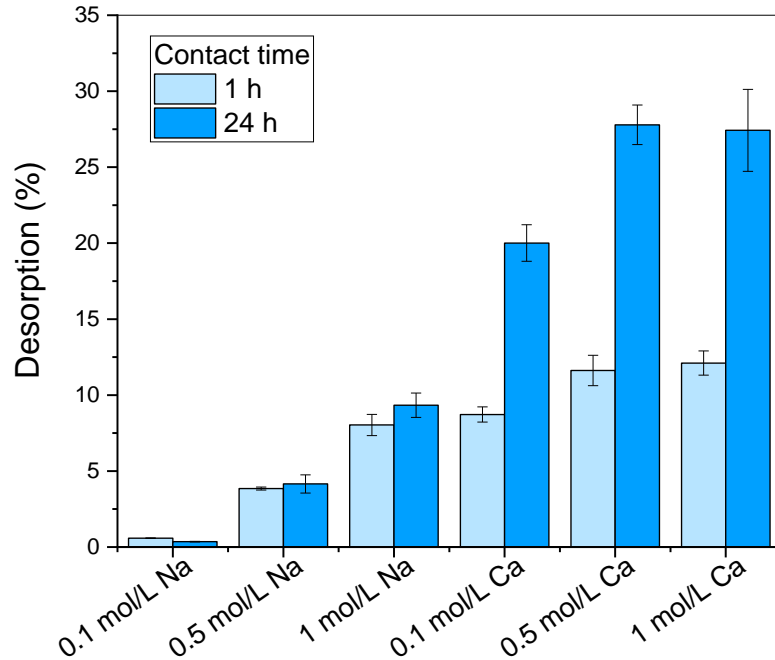
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256 **Fig. 3.** Radionuclide uptake from natural seawater (SW) using Z4A. Contact time 10 min, Z4A
 257 dose 10 g/L, shaking speed 10 rpm.

258

259 **Recovery of Sr from Z4A**

260 The method development was further focused on the recovery of Sr entrapped into Z4A crystal
 261 lattice to facilitate its separation from other cations using highly selective resins. For this purpose,
 262 the desorption efficiency of several solutions was tested, as shown in Fig 4.



263

264 **Fig. 4.** The efficiency of Sr desorption from Z4A influenced by desorbing solution composition
 265 and contact time. Solid to solution ratio 0.2 g/20 mL, shaking speed 10 rpm.

266

267 In the sorption step, the efficiency of Sr removal from SSW was 94 ± 3 % considering 24
 268 replicate tests conducted under optimized experimental conditions, confirming repeatable Sr
 269 preconcentration. Desorption of Sr was influenced by the type, the concentration of the desorbing
 270 agent, and the time of contact; however, it was generally low (Fig. 4). After 1 h, 0.58% - 8.0% and
 271 8.7 % - 12.1% of Sr were desorbed with increasing concentrations of NaCl and CaCl₂, respectively.
 272 Due to the chemical similarity with Sr, Ca ions affect the desorption of Sr more significantly than
 273 Na. Furthermore, the recovery of Sr was more influenced by the prolonged contact time (24 h)
 274 with CaCl₂ solutions (20.0% - 27.7%), than with NaCl (0.36 % - 9.99 %). The study of ⁸⁹Sr
 275 desorption from Z4A in groundwater (Ca concentration of 100.4 mg/L) revealed that the

276 desorption equilibrium was reached after nine days (0.7% desorbed) [24], corroborating that the
277 desorption of Sr radionuclides from Z4A is a substantially slower process than sorption.

278 From the presented results, it is evident that Sr ions were firmly fixed in the structure of Z4A.
279 In contrast, 10 % NaCl was used to recover Cd, Zn [31], and Be [32], sorbed by zeolite 4A.
280 Depending on their previously sorbed amounts, 65% - 76% of Cd, 65% - 80% of Zn, and
281 75 % - 87 % of Be were desorbed. The level of desorption was generally found higher when
282 solutions with higher initial concentrations of cations were used in the sorption step. Consequently,
283 the most probable reasons for the observed low Sr desorption are a low total concentration of Sr
284 in seawater and a high selectivity of the zeolite 4A structure towards Sr [24].

285 Given that efficient and rapid Sr recovery could not be achieved by desorption, another
286 approach for Sr recovery was tested – the dissolution of the Z4A framework. The Si/Al ratio of
287 the zeolite controls the dissolution rate and mechanism, as the selective Al removal constrains the
288 removal of Si [33,34]. Therefore, the dissolution of zeolites with different Si/Al ratios may result
289 in stoichiometric degradation, precipitation of silicate, partially dissolved or preserved silicate
290 framework. The acidic decomposition of zeolites may be accompanied by precipitation of
291 insoluble silica or gelatinization. The formation of a gel is characteristic of zeolites containing at
292 least two Al atoms to three Si atoms [33]. Zeolite 4A is characterized by extremely high Al content
293 (Si/Al = 1.0), and its fast and stoichiometric dissolution upon treatment with hydrochloric acid was
294 confirmed by measuring the concentrations of Al and Si in the liquid phase [34]. However, the
295 decrease in aqueous Si concentration with time was detected due to a formation of a gel. The time
296 needed for gel formation is largely dependent on the acid concentration and the volume of acid
297 applied to a given zeolite mass [33].

298 The complete dissolution of Z4A was found to occur when the pH of the solution is $\text{pH} < 0.5$.
299 In further experiments, the dissolution of Z4A was investigated in nitric acid solutions since it is
300 used for Sr loading on Sr resin or SuperLig[®]620. It was found that 10 g of Z4A can be completely
301 dissolved in 100 mL of 3 mol/L or 5 mol/L HNO₃ within 3 to 4 min, while in 2 mol/L almost
302 25 min were necessary.

303 Nevertheless, in 5 mol/L HNO₃, the gel was formed after only 40 min. This effect is
304 undesirable since it causes clogging of the column filled with Sr resin or SuperLig[®]620. The stages
305 of Z4A complete dissolution and gel formation are illustrated in Fig. S1. Using 3 mol/L HNO₃, the
306 gelatinization occurred within 24 h, while in 2 mol/L solution after three days.

307 Since the gelatinization process was slowest in 2 mol/L HNO₃, its volume was increased to
308 120 mL to examine the influence on the dissolution rate. Under such conditions, Z4A (10 g) was
309 dissolved rapidly within 5 min, which was taken as optimum for loading on SuperLig[®]620.

310 SuperLig[®]620 was selected for several reasons. Firstly, only cca. 0.4 g of Sr resin can be loaded
311 in 1 mL Supelco column, which is not enough for complete Sr binding. Tayeb et al. [11] have
312 shown that for only 100 mL of purified SW, the tandem of Sr resin (2 times 2 mL columns) was
313 necessary to improve Sr recovery, with a final recovery of 85 ± 3 %. Secondly, the advantage of
314 SuperLig[®]620 is that it is not sensitive to higher flow rates in comparison to Sr resin and
315 AnaLig[®]Sr-01 [13], which significantly reduces the time of separation. The main advantage of
316 automated separation is that by using SuperLig[®]620 multiple uses are allowed, and this material
317 has higher stability over time than Sr resin [27,35]. If Sr can be determined from smaller volumes,
318 such as 100 mL of SW, then 1 g of Z4A is necessary for Sr preconcentration, which can be
319 dissolved in only 10 mL of 3 mol/L HNO₃ or 12 mL of 2 HNO₃. In such cases, Sr resin or
320 AnaLig[®]Sr-01 might be effective for further Sr separation and determination.

321

322 **New procedure for $^{89,90}\text{Sr}$ determination in SW**

323 The scheme of a new procedure, indicating the time required to separate Sr from 1 L SW sample
324 is presented in Fig. S2. As shown, Sr was removed from 1 L of SW by 10 g of Z4A. After
325 dissolving Z4A with 120 mL of 2 mol/L HNO_3 , the solution was loaded by the automated system
326 on 1 mL SuperLig[®]620 (preconditioned with 20 mL of 2 mol/L HNO_3). The recovery of Sr,
327 determined by ^{85}Sr or ^{89}Sr in ten repetitions, was $89 \pm 4\%$ for the whole procedure.

328 By introducing the preconcentration step with Z4A before column separation, complete
329 retention of Sr on the resin was enabled, compared to no retention of Sr directly from SW. Due to
330 the fast kinetics of Sr sorption by Z4A at ambient temperature, it is possible to apply this method
331 in emergency situations. Since Z4A also retains Ba, and ^{140}Ba is expected to be present, Sr had to
332 be eluted from the column without a breakthrough of Ba. Therefore, Sr was eluted from the column
333 by 20 mL of 0.05 mol/L EDTA solution, pH ~ 6 [27], directly into the scintillation vial. The Sr
334 fraction was then counted immediately after separation to determine the activity of ^{89}Sr . ^{90}Sr was
335 determined by successive counting and after several hours by ingrowth ^{90}Y , as described earlier
336 [13,28].

337 The ratio between ^{89}Sr and ^{90}Sr is expected to be in favor of ^{89}Sr in fresh fallout, and the highest
338 ratio where simultaneously both isotopes can accurately be determined is around 17:1 [38].
339 Therefore, the model solutions with high $^{89}\text{Sr}/^{90}\text{Sr}$ activity ratios were used to validate the method.
340 In addition, the method's applicability was tested by spiking 1 L of SW with proficiency test sample
341 Analytics CC. The results demonstrated good agreement between measured and expected values,
342 as shown in Table 1.

343 In the first case, a model solution was spiked with several radionuclides. As the results in Fig.
 344 3 had demonstrated, they have been sorbed with different efficiencies on Z4A. After dissolving
 345 Z4A and separation on SuperLig[®]620, only Sr and Ba were retained on the resin, and Sr was
 346 effectively eluted ($99.5 \pm 1\%$) while Ba remained on the resin. Proficiency tests sample Analytics,
 347 which simulate routine effluent sample, except $^{89,90}\text{Sr}$, contained ^{141}Ce , $^{134,137}\text{Cs}$, $^{58,60}\text{Co}$, ^{54}Mn ,
 348 ^{59}Fe , and ^{65}Zn . Neither of them was determined in the Sr fraction. In these experiments, the
 349 recovery of Sr was taken as 89 %, and its uncertainty was included in the uncertainty budget. The
 350 relative bias of the results for the radionuclide in excess, ^{89}Sr was less than 6%, while for ^{90}Sr ,
 351 12%, which is acceptable in case of emergency. As the time between separation and counting was
 352 increased, the bias for ^{90}Sr decreased due to ingrowth of ^{90}Y decreased, and more counts were
 353 detected.

354
 355 **Table 1.** Results of $^{89,90}\text{Sr}$ determination in SW spiked with $^{89,90}\text{Sr}$ and several other radionuclides
 356 or Analytics CC proficiency test sample.

Sample	V, L	^{89}Sr , Bq/L measured	^{89}Sr , Bq/L expected	Rel. bias, %	MDA, Bq/L	^{90}Sr , Bq/L measured	^{90}Sr , Bq/L expected	Rel bias, %	MDA, Bq/L
Model solution 1	0.125	145 ± 20	147	-1.4	3.51	$11.4 \pm 3.1^*$	10.29	10.8	8.01
Model solution 2	1.0	39.9 ± 2.2	42.4	-5.9	0.74	$4.12 \pm 0.74^*$	3.70	11.4	1.47
Analytics CC	1.0	299 ± 10	296	1.0	2.07	$32.8 \pm 2.6^{**}$	34.0	-3.5	3.08

357 *38 h after separation

358 **36 h after separation

359 MDA is minimum detectable activity, calculated according to ISO 11 929

360 Uncertainties are combined statistical and systematic uncertainties at 1 sigma.

361

362 With the proposed method, 36 to 38 h after separation, which corresponds to 32-33 % of
 363 ingrowth ^{90}Y , (half-life of ^{90}Y , $t_{1/2} = 64,04$) and 30 min counting time, minimum detectable

364 activities observed were 3.51 Bq/L, 0.74 Bq/L, 2.07 Bq/L for ^{89}Sr , and 8.01 Bq/L, 1.47 Bq/L, 3.08
365 Bq/L for ^{90}Sr . As can be seen, different MDA were obtained at similar activity ratios $^{89}\text{Sr}:^{90}\text{Sr}$
366 $\sim 10:1$. In addition to the sample volume, detection efficiency, recovery, count time, and
367 background count rate, the MDA also depends on the activity concentration of the other isotope
368 present in the sample. Therefore, the MDA in model solution 1 were the highest at a sample volume
369 of 0.125 L, but by increasing the counting time to 100 min, the MDA can be decreased to 1.92
370 Bq/L for ^{89}Sr and 4.38 Bq/L for ^{90}Sr . On the other hand, the MDA for 1 L samples were lower,
371 even at higher initial activities (model solution 1 vs. Analytics CC). The results for similar initial
372 activities are comparable to those obtained by Tayeb et al. [11]. For similar activities of $^{89,90}\text{Sr}$ in
373 the sample, 295 Bq/L of ^{89}Sr and 32.5 Bq/L of ^{90}Sr , minimum detectable activities achieved were
374 2.40 Bq/L for ^{89}Sr and 3.47 Bq/L for ^{90}Sr , for 15 min counting time on Hidex SL 300 (LSC with
375 3-PMT), and 0.1 L spiked SW sample. Their MDA were likely obtained for a much smaller initial
376 volume of SW after combined Cherenkov and liquid scintillation counting, which makes the
377 procedure somewhat more complicated and increases the time required to handle the sample.
378 Under similar counting conditions as in the presented study, their MDA values would be much
379 higher. Nevertheless, both methods give good and rapid results, however, by the presented method,
380 the mean recovery of Sr is slightly higher, $89 \pm 4\%$, compared to $85.4 \pm 3.3\%$, and the
381 preconcentration step is easier to handle, especially at the sampling site.

382 By using Z4A, the zeolite was simply mixed with SW and separated. On the other hand, the
383 addition of NH_4OH and Na_2CO_3 with pH control was necessary for precipitation of carbonates,
384 which is less convenient if the preconcentration step is conducted outside the laboratory, such as
385 directly at the sampling site. In addition, by using SuperLig[®]620 resin, higher flow rates may be
386 applied, up to 5 to 10 mL/min, with no further loss of Sr using less concentrated HNO_3 . The

387 activities of $^{89,90}\text{Sr}$ can even be determined directly on site using the Triathler, a portable LSC with
388 1 PMT, in combination with the presented method. This approach would further reduce the time
389 to obtain results, which is crucial in an emergency. Due to the lower efficiency and higher
390 background counts, the MDA on Triathler is expected to be higher than for LSC with 2 or 3 PMT
391 [36], but probably low enough for accurate determination of high $^{89,90}\text{Sr}$ activities.

392 The proposed method can be further developed with the goal of determining ^{90}Sr via ^{90}Y , e.g.,
393 determination of ^{90}Y by using the DGA column. After filtration, Z4A should be stored in powder
394 form for at least 14 days to establish a secular equilibrium between ^{90}Sr - ^{90}Y . The dissolution step
395 should be performed shortly before column separation to avoid gelation of the sample with time
396 [34]. By connecting SuperLig[®]620 in series with the DGA column, ^{90}Sr was captured on the
397 SuperLig column, while ^{90}Y on 1 mL DGA column (0.4 g of the resin) with obtained recovery of
398 around 97%.

399 Uesugi et al. [7] presented a method that consists of precipitation of magnesium ammonium
400 phosphates and hydroxyapatite to concentrate Sr from 1 L of SW. The obtained deposit was
401 dissolved in 4 mol/L HNO_3 and filtrated through a tandem of Sr Rad Disks. Sr was eluted with a
402 0.5 mol/L solution of diammonium hydrogen citrate and mixed with a scintillator, which has 20%
403 solution of HDEHP to determine the Sr by liquid scintillation counting. The Sr Rad Disk may be
404 used again. Sr recovery of this method was determined using the addition of ^{85}Sr , and it was 80-
405 90%. The authors suggested that determining the chemical recovery may be unnecessary during a
406 nuclear emergency. The detection limit of 35 mBq/L for 1 L of SW was determined for 1 h
407 counting and detection efficiency of 75%. Since the method with Z4A also provides stable
408 recovery and is consistent, determining the chemical recovery may be considered unnecessary
409 during a nuclear emergency and can be taken as $89 \pm 4\%$. The material in Sr Rad Disk is

410 SuperLig[®]620, and by the approach presented here, the amount of resin is not fixed by the size of
 411 Rad Disks. Furthermore, the preconcentration of SW sample by Z4A is easier and overall
 412 separation time is much shorter, with slightly higher recoveries achieved.

413 The method was tested by using proficiency test samples of seawater provided by IAEA,
 414 Monaco, IAEA-RML-2017-01 and IAEA-RML-2021-01, and satisfactory results were obtained
 415 (Table 2). Samples were prepared as described, and the Sr fraction was repeatedly counted until a
 416 secular equilibrium between ⁹⁰Sr and ⁹⁰Y was achieved. The detection limit was determined to be
 417 29 mBq/L, for 1 L of the sample, recovery of 89%, and a counting time of 60 min.

418

Table 2. Results of ⁹⁰Sr determination in proficiency test samples IAEA-RML-2017-01 and IAEA-RML-2021-01.

PT Sample	$c_{a\text{ref}}(^{90}\text{Sr})$, Bq/L	$c_{a\text{exp}}(^{90}\text{Sr})$, Bq/L	Rel. bias, %	z - score
IAEA-RML-2017-01	0.2748 ± 0.0019	0.2648 ± 0.015	-3.64	-0.51
IAEA-RML-2021-01	0.609 ± 0.005	0.552 ± 0.041	-9.36	-1.39

419 $c_{a\text{ref}}(^{90}\text{Sr})/c_{a\text{exp}}(^{90}\text{Sr})$ – reference/experimental activity concentration of ⁹⁰Sr

420

421 As it was presented, the applicability of Z4A for the preconcentration of Sr from complex
 422 matrices, like SW, enables the development of a simple and more rapid procedure for the
 423 determination of ^{89,90}Sr. This material may be potentially used for higher volumes of SW, where
 424 low concentrations of ⁹⁰Sr are present, such as average activity concentrations of ⁹⁰Sr in SW
 425 (approximately 1 mBq/L [2]). Further research is necessary to investigate such applicability.

426

427 **Conclusion**

428 For the first time, synthetic zeolite Z4A coupled with highly selective material for Sr separation
429 was employed for radioanalytical application. The method was developed to facilitate the
430 determination of radiostrontium isotopes in complex matrices, such as seawater, which is
431 otherwise very complicated due to chemical interferences and represents a major obstacle in
432 monitoring Sr activity in case of nuclear emergencies. The proposed procedure is rapid and
433 straightforward and can even be completed directly at the sampling site. The preconcentration of
434 Sr radionuclides is performed by simply mixing zeolite Z4A with seawater at a dose of 10 g/L.
435 Since the process does not involve the addition of other chemicals, pH adjustments, and other time-
436 consuming steps, it provides significant advantages over existing techniques in terms of speed and
437 simplicity. The complete preparation of the sample, including zeolite 4A dissolution and Sr
438 separation on a highly selective resin, takes less than 1.5 h. The recovery of Sr following the entire
439 procedure is high, consistent, and stable ($89 \pm 4\%$). The obtained results have shown that in case
440 of emergency, where high activity ratio $^{89}\text{Sr}:^{90}\text{Sr}$ is expected, activities of both isotopes may be
441 determined with satisfactory accuracy. Additionally, results obtained from IAEA seawater samples
442 have shown that method was successfully employed to determine lower activity concentrations of
443 ^{90}Sr , where MDA of 29 mBq/L was achieved. Further research would result in novel cognition of
444 possible uses and improvements of the proposed analytical concept.

445

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451

452 **Appendix A. Supplementary data**

453 Supplementary data to this article can be found online at

454

455 **References**

- 456 [1] N. Casacuberta, P. Masqué, J. Garcia-Orellana, R. Garcia-Tenorio, K.O. Buesseler, ^{89}Sr and
457 ^{90}Sr in seawater off Japan as a consequence of the Fukushima Dai-ichi nuclear accident,
458 *Biogeosciences* 10 (2013) 3649–3659. <https://doi.org/10.5194/bg-10-3649-2013>.
- 459 [2] P.P. Povinec, K. Hirose, M. Aoyama, Radiostrontium in the Western North Pacific:
460 characteristics, behavior, and the Fukushima impact, *Environ. Sci. Technol.* (2012)
461 120827130423002. <https://doi.org/10.1021/es301997c>.
- 462 [3] M. Castrillejo, N. Casacuberta, C.F. Breier, S.M. Pike, P. Masqué, K.O. Buesseler,
463 Reassessment of ^{90}Sr , ^{137}Cs , and ^{134}Cs in the coast off Japan derived from the Fukushima
464 Dai-ichi nuclear accident, *Environ. Sci. Technol.* 50 (2016) 173–180.
465 <https://doi.org/10.1021/acs.est.5b03903>.
- 466 [4] R. Querfeld, A.E. Pasi, K. Shozugawa, C. Vockenhuber, H.A. Synal, P. Steier, G.
467 Steinhauser, Radionuclides in surface waters around the damaged Fukushima Daiichi NPP
468 one month after the accident: evidence of significant tritium release into the environment,
469 *Sci. Total Environ.* 689 (2019) 451–456. <https://doi.org/10.1016/j.scitotenv.2019.06.362>.
- 470 [5] U.S. Department of Health and Human Services, Public Health Service, Agency for Toxic
471 Substances and Disease Registry: Toxicological profile of strontium (2004).
472 <https://www.atsdr.cdc.gov/toxprofiles/tp159.pdf> (accessed 24 Jan 24, 2019).

- 473 [6] Q. Chen, X. Hou, Y. Yu, H. Dahlgaard, S.P. Nielsen, Separation of Sr from Ca, Ba and Ra
474 by means of $\text{Ca}(\text{OH})_2$ and $\text{Ba}(\text{Ra})\text{Cl}_2$ or $\text{Ba}(\text{Ra})\text{SO}_4$ for the determination of radiostrontium,
475 *Anal. Chim. Acta* 466 (2002) 109–116. [https://doi.org/10.1016/S0003-2670\(02\)00571-8](https://doi.org/10.1016/S0003-2670(02)00571-8).
- 476 [7] M. Uesugi, R. Watanabe, H. Sakai, A. Yokoyama, Rapid method for determination of ^{90}Sr
477 in seawater by liquid scintillation counting with an extractive scintillator, *Talanta* 178
478 (2018) 339–347. <https://doi.org/10.1016/j.talanta.2017.09.041>.
- 479 [8] S.L. Maxwell, B.K. Culligan, R.C. Utsey, Rapid determination of radiostrontium in
480 seawater samples, *J. Radioanal. Nucl. Chem.* 298 (2013) 867–875.
481 <https://doi.org/10.1007/s10967-013-2430-1>.
- 482 [9] H. Tazoe, H. Obata, T. Yamagata, Z. Karube, H. Nagai, M. Yamada, Determination of
483 strontium-90 from direct separation of yttrium-90 by solid phase extraction using DGA
484 Resin for seawater monitoring, *Talanta* 152 (2016) 219–227.
485 <https://doi.org/10.1016/j.talanta.2016.01.065>.
- 486 [10] M. Tayeb, X. Dai, E.C. Corcoran, D.G. Kelly, Rapid determination of ^{90}Sr from ^{90}Y in
487 seawater, *J. Radioanal. Nucl. Chem.* 304 (2015) 1043–1052.
488 <https://doi.org/10.1007/s10967-015-3935-6>.
- 489 [11] M. Tayeb, X. Dai, S. Sdraulig, Rapid and simultaneous determination of Strontium-89 and
490 Strontium-90 in seawater, *J. Environ. Radioact.* 153 (2016) 214–221.
491 <https://doi.org/10.1016/j.jenvrad.2016.01.003>.
- 492 [12] Ž. Grahek, M.R. Mačefat, Determination of radioactive strontium in seawater, *Anal. Chim.*
493 *Acta* 534 (2005) 271–279. <https://doi.org/10.1016/j.aca.2004.11.050>.

- 494 [13] I. Milanović, Ž. Grahek, Semi-automated procedure for the determination of $^{89,90}\text{Sr}$ in
495 environmental samples by Cherenkov counting, *J. Radioanal. Nucl. Chem.* 303 (2015)
496 1453–1457. <https://doi.org/10.1007/s10967-014-3614-z>.
- 497 [14] Ž. Grahek, I. Eškinja, K. Košutic, S. Lulic, K. Kvastek, Isolation of radioactive strontium
498 from natural samples: separation of strontium from alkaline and alkaline earth elements by
499 means of mixed solvent anion exchange, *Anal. Chim. Acta* 379 (1999) 107–119.
500 [https://doi.org/10.1016/S0003-2670\(98\)00655-2](https://doi.org/10.1016/S0003-2670(98)00655-2).
- 501 [15] H. Tazoe, H. Obata, M. Tomita, S. Namura, J. Nishioka, T. Yamagata, Z. Karube, M.
502 Yamada, Novel method for low level Sr-90 activity detection in seawater by combining
503 oxalate precipitation and chelating resin extraction, *Geochem. J.* 51 (2017) 193–197.
504 <https://doi.org/10.2343/geochemj.2.0441>.
- 505 [16] D. Alby, C. Charnay, M. Heran, B. PreLOT, J. Zajac, Recent developments in nanostructured
506 inorganic materials for sorption of cesium and strontium: synthesis and shaping, sorption
507 capacity, mechanisms, and selectivity—A review, *J. Hazard. Mater.* 344 (2018) 511–530.
508 <https://doi.org/10.1016/j.jhazmat.2017.10.047>.
- 509 [17] K.K.S. Pillay, A review of the radiation stability of ion exchange materials, *J. Radioanal.*
510 *Nucl. Chem.* 102 (1986) 247–268. <https://doi.org/10.1007/BF02037966>.
- 511 [18] R.O. Abdel Rahman, H.A. Ibrahim, Y.T. Hung, Liquid radioactive wastes treatment: a
512 review, *Water* 3 (2011) 551–565. <https://doi.org/10.3390/w3020551>.
- 513 [19] A.M. El-Kamash, Evaluation of zeolite A for the sorptive removal of Cs^+ and Sr^{2+} ions from
514 aqueous solutions using batch and fixed bed column operations, *J. Hazard. Mater.* 151
515 (2008) 432–445. <https://doi.org/10.1016/j.jhazmat.2007.06.009>.

- 516 [20] Y. Li, L. Li, J. Yu, Applications of zeolites in sustainable chemistry, *Chem* 3 (2017) 928–
517 949. <https://doi.org/10.1016/j.chempr.2017.10.009>.
- 518 [21] H. Faghihian, M. Iravani, M. Moayed, M. Ghannadi-Maragheh, Preparation of a novel
519 PAN-zeolite nanocomposite for removal of Cs⁺ and Sr²⁺ from aqueous solutions: Kinetic,
520 equilibrium, and thermodynamic studies, *Chem. Eng. J.* 222 (2013) 41–48.
521 <https://doi.org/10.1016/j.cej.2013.02.035>.
- 522 [22] A. Merceille, E. Weinzaepfel, Y. Barré, A. Grandjean, The sorption behaviour of synthetic
523 sodium nonatitanate and zeolite A for removing radioactive strontium from aqueous wastes,
524 *Sep. Purif. Technol.* 96 (2012) 81–88. <https://doi.org/10.1016/j.seppur.2012.05.018>.
- 525 [23] H. Faghihian, M. Moayed, A. Firooz, M. Iravani, Synthesis of a novel magnetic zeolite
526 nanocomposite for removal of Cs⁺ and Sr²⁺ from aqueous solution: Kinetic, equilibrium,
527 and thermodynamic studies, *J. Colloid Interface Sci.* 393 (2013) 445–451.
528 <https://doi.org/10.1016/j.jcis.2012.11.010>.
- 529 [24] I. Smičiklas, I. Cocha, M. Jović, M. Nodilo, M. Šljivić-Ivanović, S. Smiljanić, Ž. Grahek,
530 Efficient separation of strontium radionuclides from high-salinity wastewater by zeolite 4A
531 synthesized from Bayer process liquids, *Sci. Rep.* 11 (2021) 1738.
532 <https://doi.org/10.1038/s41598-021-81255-y>.
- 533 [25] O. Halevi, T.-Y. Chen, P.S. Lee, S. Magdassi, J.A. Hriljac, Nuclear wastewater
534 decontamination by 3D-Printed hierarchical zeolite monoliths, *RSC Adv.* 10 (2020) 5766–
535 5776. <https://doi.org/10.1039/C9RA09967K>.
- 536 [26] Perkin-Elmer, Analytical methods for atomic absorption spectroscopy, Manual Part No.
537 0303-0152 Release D. Perkin-Elmer Corporation, Waltham, MA, 1996.

- 538 [27] I. Cocha, S. Dulanská, I. Tucaković, Ž. Grahek, Synergy of flow injection system and
539 molecular recognition technology products for rapid determination of $^{89,90}\text{Sr}$ and ^{210}Pb ,
540 *Talanta* 225 (2021) 121959. <https://doi.org/10.1016/j.talanta.2020.121959>.
- 541 [28] Ž. Grahek, M. Nodilo, G. Karanović, Rapid determination of $^{89,90}\text{Sr}$ in wide range of activity
542 concentration by combination of yttrium, strontium separation and Cherenkov counting, *J.*
543 *Radioanal. Nucl. Chem.* 292 (2012) 555–569. <https://doi.org/10.1007/s10967-011-1441-z>.
- 544 [29] International Organization for Standardization, ISO 11929:2010 - Determination of the
545 characteristic limits (decision threshold, detection limit and limits of the confidence
546 interval) for measurements of ionizing radiation - Fundamentals and application,
547 <https://www.iso.org/standard/43810.html> (accessed 9 Aug, 2017).
- 548 [30] The Royal Society, Ocean acidification due to increasing atmospheric carbon dioxide,
549 Policy document 12/0, 2005. [https://royalsociety.org/-](https://royalsociety.org/-/media/Royal_Society_Content/policy/publications/2005/9634.pdf)
550 [/media/Royal_Society_Content/policy/publications/2005/9634.pdf](https://royalsociety.org/-/media/Royal_Society_Content/policy/publications/2005/9634.pdf) (accessed 12 Oct,
551 2021).
- 552 [31] G. Purna Chandra Rao, S. Satyaveni, A. Ramesh, K. Sessaiah, K.S.N. Murthy, N.V.
553 Choudary, Sorption of cadmium and zinc from aqueous solutions by zeolite 4A, zeolite 13X
554 and bentonite, *J. Environ. Manag.* 81 (2006) 265–272.
555 <https://doi.org/10.1016/j.jenvman.2005.11.003>.
- 556 [32] A. Ramesh, K.R. Mohan, K. Sessaiah, N.V. Choudary, Removal of beryllium from aqueous
557 solutions by zeolite 4A and bentonite, *Sep. Sci. Techn.* 37 (2002) 1123–1134.
558 <https://doi.org/10.1081/SS-120002245>.
- 559 [33] K.J. Murata, Internal structure of silicate minerals that gelatinize with acid, *Am. Mineral.*

560 28 (1943) 545–562.

561 [34] R.L. Hartman, H.S. Fogler, Understanding the dissolution of zeolites, *Langmuir*. 23 (2007)
562 5477–5484. <https://doi.org/10.1021/la063699g>.

563 [35] J.S. Bradshaw, R.L. Bruening, K.E. Krakowiak, B.J. Tarbet, M.L. Bruening, R.M. Izatt, J.J.
564 Christensen, Preparation of silica gel-bound macrocycles and their cation-binding
565 properties, *J. Chem. Soc., Chem. Commun.* (1988) 812–814.
566 <https://doi.org/10.1039/c39880000812>.

567 [36] I. Cocha, S. Neufuss, Ž. Grahek, M. Němec, M. Nodilo, J. John, The effect of counting
568 conditions on pure beta emitter determination by Cherenkov counting, *J. Radioanal. Nucl.*
569 *Chem.* 310 (2016) 891–903. <https://doi.org/10.1007/s10967-016-4853-y>.