



Rapid determination of ^{129}I in large-volume water samples using rotary evaporation preconcentration and accelerator mass spectrometry measurement

Li, Jing; Zhang, Luyuan; Hou, Xiaolin; Cheng, Peng; Chen, Ning; Yu, Xia; Liu, Qi; Fan, Yukun

Published in:
Journal of Radioanalytical and Nuclear Chemistry

Link to article, DOI:
[10.1007/s10967-018-6180-y](https://doi.org/10.1007/s10967-018-6180-y)

Publication date:
2018

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):
Li, J., Zhang, L., Hou, X., Cheng, P., Chen, N., Yu, X., Liu, Q., & Fan, Y. (2018). Rapid determination of ^{129}I in large-volume water samples using rotary evaporation preconcentration and accelerator mass spectrometry measurement. *Journal of Radioanalytical and Nuclear Chemistry*, 318(3), 2355-2361.
<https://doi.org/10.1007/s10967-018-6180-y>

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

1 **Rapid determination of iodine-129 in large-volume water samples using rotary**
2 **evaporation preconcentration and accelerator mass spectrometry measurement**

3 Jing Li ^{1,4}, Luyuan Zhang ^{1,3*}, Xiaolin Hou ^{1,2,3}, Peng Cheng ^{1,3}, Ning Cheng ¹,

4 Xia Yu ^{1,4}, Qi Liu ¹, Yukun Fan ¹

5 ¹ *State Key Laboratory of Loess and Quaternary Geology, Shaanxi Key Laboratory of*
6 *Accelerator Mass Spectrometry and Application, Xi ' an AMS Center, Institute of Earth*
7 *Environment, Chinese Academy of Sciences, Xi ' an 710061, China*

8 ² *Center for Nuclear Technologies, Technical University of Denmark, Risø Campus,*
9 *Roskilde 4000, Denmark*

10 ³ *Open Studio for Oceanic-Continental Climate and Environment Changes, Pilot*
11 *National Laboratory for Marine Science and Technology (Qingdao), Qingdao 266061,*
12 *China*

13 ⁴ *University of Chinese Academy of Science, Beijing 100049, China*

14

15 E-mail: zhangly@ieecas.cn; houxl@ieecas.cn

16 **Abstract**

17 A rapid method using rotary evaporation combined with accelerator mass spectrometry
18 (AMS) measurement, was developed for the determination of ¹²⁹I in large-volume water
19 samples. The parameters including water bath temperature, pH, concentration volume
20 and reducing reagent, were thoroughly optimized. The chemical yield of iodine under the

21 optimal conditions is between 98.8 and 100.7%. Compared to the direct evaporation, the
22 enrichment time can be shortened by five times. The measured $^{129}\text{I}/^{127}\text{I}$ ratios for the
23 environmental water samples are in good agreement with those previously reported
24 values, suggesting this method is accurate, robust and suitable for ^{129}I determination in
25 large water samples.

26 **Keywords**

27 ^{129}I , Large-volume, Water samples, Rotary evaporation, Accelerator mass spectrometry

28 **Introduction**

29 Iodine has only one stable isotope, ^{127}I and the only long-lived radionuclide is ^{129}I
30 (half-life of 15.7 Ma) [1]. ^{129}I is naturally generated via cosmic ray reactions with xenon
31 in the upper atmosphere, spontaneous fission of ^{238}U and thermal neutron-induced fission
32 of ^{235}U in the earth (with a total inventory of 250 kg in the environment).

33 The sources of ^{129}I in the environment are currently dominated by human activities,
34 with a total inventory of approximately 6100 kg released mainly by reprocessing of
35 nuclear fuel as of 2009 [2, 3]. The anthropogenic ^{129}I has dispersed to large area, $^{129}\text{I}/^{127}\text{I}$
36 ratios in the environment have increased by 1 to 6 orders of magnitude compared to the
37 level in the pre-nuclear age [4-6]. The conservative behavior in oceans and the
38 physicochemical properties of iodine, as well as the long half-life, make ^{129}I ideal for
39 many applications, such as tracing the movement and exchange of water masses in the
40 seas [7, 8], tracing the atmospheric behavior and process of iodine [9], providing

41 knowledge on geochemical cycling of stable iodine [10, 11], tracing the migration of
42 organic matter and age dating of marine geological events between 2 and 80 Ma [12-15].

43 Natural ^{129}I is ideal as a hydrologic tracer owing to being soluble and highly mobile
44 in any hydrologic environment [16]. Fabryka-Martin et al. [16] have presented ^{129}I data in
45 ground water samples collected from the Great Artesian Basin, Australia. Along with
46 other hydrogeological evidence, this work suggests large-scale mixing of waters between
47 Cretaceous and Jurassic formations, intrusion of atmospheric iodine to the groundwater
48 and in-situ production of ^{129}I from an underlying formation significantly higher in
49 uranium content. Despite this high potential, applications of ^{129}I in hydrogeological
50 system have so far been limited, because it generally needs large-volume water samples.
51 At least 1 mg of stable iodine (^{127}I) is required for a measurement, but the environment
52 concentration of ^{127}I is very low, for example, only 1-10 $\mu\text{g/L}$ of iodine are present in
53 meteoric, surface and ground water [17]. A large amount of sample is also needed for the
54 analysis of pre-nuclear samples. For instance, the analysis of a freshwater sample with
55 ^{127}I concentration of 5 $\mu\text{g/L}$, and an $^{129}\text{I}/^{127}\text{I}$ ratio of 10^{-12} , requires at least 10 L sample to
56 obtain a reliable measurement results. Thus, pre-concentration of iodine from water
57 samples is necessary. The methods are mainly anion exchange chromatography, direct
58 evaporation by heating and rotary evaporation. Anion exchange chromatography is
59 relatively complicated, time-consuming with more than 12h for 10 L water sample, and
60 suffer from low iodine recovery of about 50-87% [18]. Direct evaporation at sub-boiling
61 conditions is conventionally used, giving a high iodine recovery (>90%) but also taking a
62 long time. For instance, it takes more than 20 h to concentrate a water sample from 5 L to
63 1 L [19, 20]. Rotary evaporation method is operated under pressure for continuous

64 distillation of volatile solvents, with the advantage of being fast and efficient. This
65 method has been used for freshwater samples from the orange county aquifer system,
66 California, and 40 rivers of the USA, Canada and Western Europe [21-23]. However, it is
67 not clear so far whether the rotary evaporation process cause iodine a loss, and to what
68 extent it will influence the chemical yield of iodine.

69 This work aims to investigate the influence and corresponding mechanisms of the
70 various rotary evaporation parameters on the recovery rate of iodine, and to obtain
71 optimal operation conditions for rapid determination of ^{129}I in large-volume water
72 samples. Finally, the optimized experimental conditions were applied to the
73 determination of ^{129}I in several environmental water samples.

74 **Experimental**

75 **Samples, chemicals and instruments**

76 Four water samples were analyzed in this study. Two rainfall samples were collected
77 on the roof of the Xi'an Accelerator Mass Spectrometry Center (34°13'25.23"N,
78 108°59'58.89"E) on 8th December, 2015, and stored in PE containers in dark until
79 analysis. A lake water sample was collected from a public garden in the center of Xi'an
80 (34°15'17"N,108°58'38"E) on 2nd September, 2017, and stored in an airtight
81 polyethylene container. An underground water sample was collected in Hancheng of
82 Shaanxi province (35°28'45.9"N, 110°23'41.1"E), and stored in dark until analysis.

83 All chemical reagents used in this work are of analytical grade, mainly including
84 NaHSO_3 , HNO_3 , NaNO_2 , AgNO_3 , $\text{K}_2\text{S}_2\text{O}_8$ and NaOH purchased from Sinopharm
85 Chemical Reagent Co., Ltd (China). Iodine carrier with an $^{129}\text{I}/^{127}\text{I}$ atomic ratio of 2×10^{-14}

86 was obtained from Woodward Company (USA). ^{129}I standard solution (NIST-SRM-
87 4949C from the National Institute of Standard and Technology, Gaithersburg, MD, USA)
88 was used to prepare ^{129}I standards for the AMS measurement. Na^{125}I solution (Chengdu
89 Gaotong isotope corporation, China) was used as a tracer. Niobium powders (325 mesh,
90 99.9%) was purchased from Alfa Aesar Company (Ward Hill, MA, USA). All solutions
91 were prepared using deionized water of 18.2 M Ω /cm, produced by Cascada TM Lab
92 Water System (Pall Life Sciences, USA).

93 The rotary evaporation system consists of a rotary evaporator (RE-52AA, Shanghai
94 Yarong Biochemical Instrument Factory, China), a circulating vacuum pump (SHB,
95 Zhengzhou Great Wall science and technology co. Ltd) and a low-temperature coolant
96 circulation pump (DLSB-5/20, Zhengzhou great wall science and technology co. Ltd). A
97 gamma counter (Model FJ2021, Xi'an Nuclear Instrument Factory, China) was for ^{125}I
98 decay counting for the calculation of the chemical yield. A 3 MV Tandetron AMS
99 (HEVV, The Netherlands) at the Xi'an AMS Center was employed to determine ^{129}I . An
100 inductively coupled plasma mass spectrometry (ICP-MS) (Agilent 8800, USA) was used
101 to measure stable ^{127}I .

102 **Iodine enrichment using rotary evaporation**

103 In a first experiment 1L deionized water was transferred to a rotary evaporator. 500
104 Bq of ^{125}I was added, and then deionized water was preconcentrated by rotary vacuum
105 distillation. In this work, the concentration process was optimized by investigating the
106 effect of various parameters, including water bath temperature (50-80 °C), pH of sample
107 solution (7-13), reductant concentration (0-10 mmol/L) and final concentration volume

108 (10-120 mL). After concentration, 1 mL of water samples was taken to count ^{125}I for
109 calculating the chemical yield of iodine. Three replicates were done for each experiment.

110 **Separation of iodine from samples**

111 Water samples were filtered through a 0.45 μm membrane to remove the suspended
112 particulate matter. 1 mL of the filtered sample was taken for the determination of total
113 iodine (^{127}I). Large-volume water samples (1-5 L) were preconcentrated by the rotary
114 evaporation system. After iodine enrichment, $\text{K}_2\text{S}_2\text{O}_8$ was added to a final concentration
115 of 30 g/L. The sample was then incubated at 60°C for 20 h to decompose organic
116 substances, and for converting organic iodine into inorganic form [24]. The samples were
117 transferred to a separation funnel for solvent extraction. 1 mg of iodine carrier, 200 Bq of
118 ^{125}I tracer and 2-3 mL of 1 mol/L NaHSO_3 were added. After thoroughly mixing, 3.0
119 mol/L HNO_3 was added to adjust the pH to 1 to 2, and 15 mL of CCl_4 was added, and 2-4
120 mL of 1 mol/L NaNO_2 solution to oxidize iodide to I_2 . The formed molecular iodine (I_2)
121 was then extracted into the CCl_4 phase by shaking. After transferring CCl_4 from the
122 funnel to a beaker, a second 10-15 mL of new CCl_4 was added to the funnel to extract the
123 remaining iodine. The CCl_4 phases were combined and transferred to a new separation
124 funnel. 10 mL of H_2O and 0.5-1.0 mL of 0.1 mol/L NaHSO_3 solution were added for
125 back extraction of iodine. The extraction and back-extraction process was repeated once
126 more. After removal of the CCl_4 phase, the water phase was transferred to a 15 mL
127 centrifuge tube. ^{125}I in the separated solution in the centrifuge tube was counted using the
128 gamma detector, and the recovery of iodine in the separation procedure was calculated by
129 comparing the ^{125}I count in the samples to those in a ^{125}I standard solution with the same
130 volume. After ^{125}I measurement, 1.0 mL of 1.0 mol/L AgNO_3 was added to the separation

131 solution in the centrifuge tube to precipitate iodide as AgI. The separation AgI was
132 washed using deionized water, and the separated AgI was dried at 60°C for 2-3 h. After
133 ground to fine powder, 3 times (by weight) niobium powder was weight and mixed with
134 the AgI powder, the mixture was pressed into a copper holder for the AMS measurement
135 of $^{129}\text{I}/^{127}\text{I}$ ratio.

136 **Determination of ^{129}I and ^{127}I**

137 $^{129}\text{I}/^{127}\text{I}$ atomic ratios in the prepared targets were measured by AMS using the 3MV
138 tandem AMS system (HVVEE) at the Xi'an AMS center. I^- ions sputtered from the ion
139 source were accelerated and passed through a stripper to strip off several electrons of
140 iodine. I^{5+} was chosen for the measurement, consequently $^{127}\text{I}^{5+}$ was measured as charges
141 (current) using a Faraday cup and $^{129}\text{I}^{5+}$ was measured using a gas ionization detector.
142 The sample was measured for 6 cycles, and each sample for 5 min in each cycle.

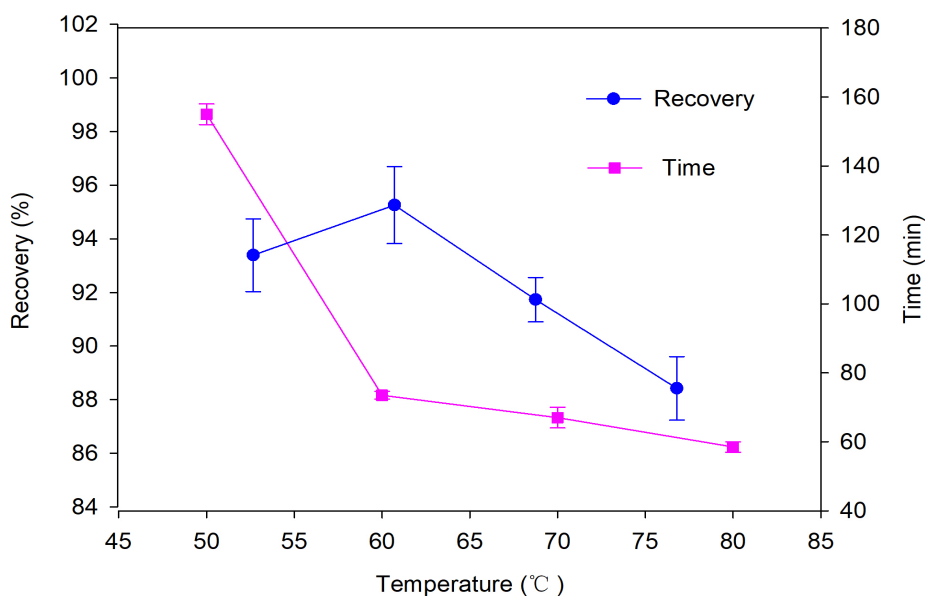
143 Total iodine (^{127}I) concentrations in water samples were measured by ICP-MS using
144 an Agilent 8800 ICP-MS (Thermal Electron Corporation), under hot plasma conditions
145 (RF of 1500 W), with the Xt interface. 10 mL filtered water was diluted by an appropriate
146 factor using 0.5% Tetramethylammonium hydroxide (TMAH) solution, and $^{133}\text{Cs}^+$ (CsCl)
147 was spiked as internal standard to a concentration of 2.0 ng/mL.

148 **Results and discussion**

149 **Effect of water bath temperature on recovery and evaporation time**

150 Water bath temperature is one of the parameters to determine distillation speed, which
151 was investigated from 50°C to 80°C by using deionized water with addition of ^{125}I tracer.

152 The results show that chemical yield of iodine increases with temperature increasing from
153 50°C to 60°C, and then decreases from 60°C to 80°C, with a peak value of $95.3\pm 1.43\%$ at
154 60°C (Fig. 1). The chemical reaction rate of iodide oxidation in aqueous solution is
155 affected by the temperature [25]. The oxidation rate will increase with increasing
156 temperature. Therefore, the lower recovery of iodine at higher temperature might be
157 attributed to the formation of volatile iodine species (e.g. HIO, I₂) [26, 27]. In contrast, a
158 relatively lower recovery was observed at 50°C, which might be attributed to long
159 evaporation time [28], approximately two times longer as that at 60°C (Fig. 1). The
160 evaporation time to concentrate from 1 L to 100 mL is greatly reduced from 155.0 ± 3.0
161 min at 50°C to 58.5 ± 1.5 min at 80°C. For 60°C, with optimal recovery of iodine, about
162 73.5 ± 1.1 min is necessary. Base on both evaporation time and iodine recovery, 60°C is
163 selected as the optimal water bath temperature.



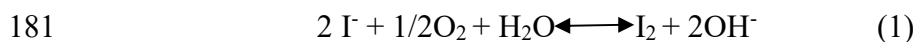
164

165 **Fig.1** Effect of water bath temperature on iodine recovery and evaporation time.(The
166 sample is deionized water with addition of ^{125}I ; Initial water volume, 1 L; Final
167 concentrated volume, 100 mL).

168 **Effect of pH on recovery of iodine**

169 Even with the optimal water bath temperature (60°C), there is still a 5% loss of iodine,
170 which might be attributed to the pH of sample solution and formation of volatile iodine
171 species. The experiment above was conducted using a neutral solution. Iodide is more
172 stable under alkaline conditions [29], thus, the effect of solution pH is investigated by
173 adjusting from 7 to 13.

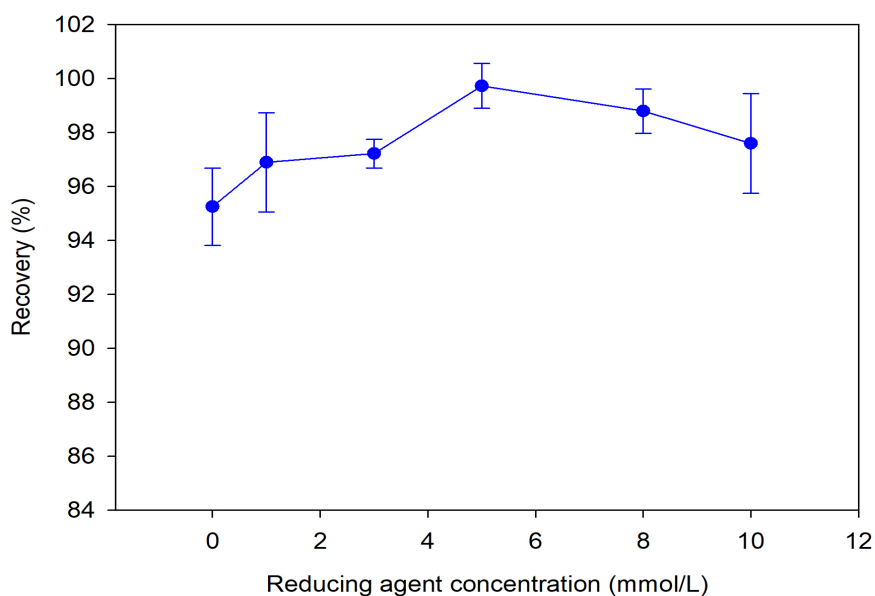
174 The results show recovery of iodine in the range of 94-95% and no significant
175 change was found (Table 1). Increase in pH and decrease in the redox potential could
176 reduce the formation of volatile iodine [30-33]. However, in alkaline solution, the
177 electrode potential of O_2 is higher than the electrode potential of I^- , so iodine redox
178 reaction can still occur (Eq.(1))[3, 33]. Since the experiment was carried out under
179 vacuum, volatile iodine species escape more easily, and the chemical reaction was push
180 to the right of the equation. Therefore, pH 7 was selected as the optimal pH value.



182 **Effect of reductant concentration on recovery of iodine**

183 Alternatively, addition of a reducing agent may inhibit iodine loss caused by formation of
184 volatile species. The effects of NaHSO_3 addition on the recovery of iodine were
185 investigated in a water bath at 60°C and $\text{pH}=7$. The reductant concentrations in the sample
186 solution were set at 1 mmol/L, 3 mmol/L, 5 mmol/L, 10 mmol/L. As shown in Fig.2, with

187 the increase of reducing agent from 0 to 5 mM, the recovery of iodine increased from
188 95.3±1.4% to 99.5±0.8%, followed by a slightly decrease when the reducing agent
189 concentration was more than 5 mmol/L. The results suggest that addition of reductant
190 could effectively inhibit the oxidation of I⁻ to HIO/I₂ and avoid iodine loss. During the
191 experiment, it was observed that when the reductant concentration increases, a large
192 amount of bubbles appear during distillation. Therefore, it can be speculated that the
193 decrease in recovery might be attributed to decomposition of NaHSO₃ to produce SO₂
194 gas, which promotes the reaction of I⁻ in the solution with O₂ in the distillation flask and
195 thus reduces the recovery of iodine.



196

197 **Fig.2** Effect of reductant concentration on iodine recovery. (Sample: deionized water;
198 Water bath temperature, 60°C; Initial water volume, 1 L; Final concentrated volume, 100
199 mL; pH =7).

200 **Effect of final concentrated volume on iodine recovery**

201 The water was concentrated to a final volume of 120 mL, 100 mL, 50 mL, 20 mL and 10
 202 mL at a water bath temperature of 60 °C, pH of 7 and a NaHSO₃ concentration of 5
 203 mmol/L. As shown in Table 1, when the volume was concentrated from 120 mL to 100
 204 mL, there is basically no iodine loss ($99.7 \pm 1.3\%$ and $99.5 \pm 0.8\%$). When the final
 205 concentrated volume was reduced from 100 mL to 10 mL, iodine recovery gradually
 206 decreased. This is because the time required for concentrating the water sample to a
 207 smaller volume gradually increases. In a same water bath temperature, the longer the
 208 time, the lower the efficiency of iodine recovery [28]. In summary, 100 ml is selected as
 209 the optimal final concentrated volume.

210 **Table 1** Effect of pH (Group 1) and concentrated volume (Group 2) on iodine recovery*

pH	Group 1			Group 2		
	Initial volume (mL)	Concentrated volume (mL)	Recovery (%)	Concentrated volume (mL)	Initial volume (mL)	Recovery (%)
7	1000	100	95.3±1.4	10	1000	95.2±0.5
8	1000	100	94.4±0.8	20	1000	95.6±1.4
11	1000	100	94.0±0.6	50	1000	97.3±1.1
13	1000	100	95.3±1.3	100	1000	99.5±0.8
				120	1000	99.7±1.3

211 * Group 1: Effect of pH on iodine recovery. (Sample: Deionized water; Water bath temperature,
 212 60°C; pH adjustment is performed by NaOH); Group 2: Effect of concentrated volume on iodine
 213 recovery (Sample: Deionized water; Water bath temperature, 60°C; pH=7; Reductant concentration,
 214 5mmol/L).

215

216 With the optimal experimental conditions obtained above, environmental fresh water
217 samples were analyzed for ^{129}I , including rain, lake and ground water samples.

218 The chemical yields of iodine among these samples are shown in Table 2. At the
219 same initial volume (1 L), a slightly lower recovery of iodine of 93.3-95.5% was
220 observed for the real environmental water samples in comparison to deionized water
221 (99.5±0.8 %). This difference might be caused by the presence of organic matter in rain
222 and lake water. The content of dissolved organic matter in rainwater was reported to be
223 0.33-31.58 mg/L [34]. In the process of rotary evaporation, the organic matter in the
224 water sample reacts with the reducing agent to consume a part of the reducing agent,
225 weakened the reducing effect of the reducing agent on I_2 , so that the actual iodine
226 recovery of the water sample is lower than that of the deionized water. For ground water,
227 a recovery of 89.0 ± 2.4 % was achieved for a 5 L sample. The 5 L water was equally
228 divided into five aliquots. The first 1 L water was preconcentrated to a volume of 200
229 mL, and then added another 1 L water sample until the total of 5 L water was finally
230 concentrated to 100 mL. For each 1 L water sample, the recovery of iodine can be
231 calculated to be 97.7% by extracting the quintic root, which is comparable with the
232 recovery for deionized water. This also confirms the influence of organic matter in real
233 water samples. In addition, rain water samples were subjected to experiments comparing
234 recovery with and without addition of reducing agent. The recoveries are 95.4±0.4% and
235 93.3±1.3% in the presence and absence of reductant, respectively. The result shows that
236 the addition of reducing agent slightly improves the recovery of iodine in real water
237 samples. Iodine in less than 1 L rainwater samples can be directly separated and purified

238 by solvent extraction [3, 35, 36]. However, for samples over 1 L, the low phase volume
 239 ratio in the extraction process results in recovery of less than 85%, and is highly organic
 240 solvent-consuming, time-consuming and labor-intensive. In this case, the sample is
 241 firstly concentrated and then subjected to solvent extraction or direct precipitation. The
 242 advantage is obvious: small sample size, easy to operate, shortened time, less organic
 243 solvent used and high recovery of iodine (>90%).

244 As shown in Table 2, the traditional heating plate evaporation method takes more
 245 than 20 hours to concentrate 5L water samples to 1L, rotary evaporation only 5 hours
 246 from 5 L to 0.1 L, indicating that the rotary evaporation method can greatly reduce
 247 sample preparation time at least 4 times.

248 The analytical results of $^{129}\text{I}/^{127}\text{I}$ atomic ratios in two rainwater, one lake water and
 249 one ground water samples are shown in Table 2. The $^{129}\text{I}/^{127}\text{I}$ ratios are $(23.5\pm 2.4) \times 10^{-10}$
 250 and $(24.5\pm 2.5) \times 10^{-10}$ for rain water samples with and without addition of reductant,
 251 respectively, $(5.67\pm 0.28) \times 10^{-10}$ for lake water, and $(0.1\pm 0.05) \times 10^{-10}$ for ground water.
 252 These results are in good agreement with those published in our previous work [19, 20,
 253 37], indicating that the rotary evaporation method is accurate, time saving and suitable
 254 for ^{129}I analysis of large-volume environmental water samples.

255 **Table 2** Analytical performance and results of $^{129}\text{I}/^{127}\text{I}$ atomic ratios in environmental
 256 water samples.

Sample	Sampling location	Method s*	Initial	Final	Time (h)	Recover	$^{129}\text{I}/^{127}\text{I}$	$^{129}\text{I}/^{127}\text{I}$
			Volume (mL)	concentrated volume (mL)		y (%)	($\times 10^{-10}$) this work	($\times 10^{-10}$) in Refs.

Rain	Xi'an	1	1000	100	1.2	95.4±0.4	23.5±2.4	24.6±2.1 ^[37]
Rain	Xi'an	1	1000	100	1.2	93.3±1.3	24.5±2.5	24.6±2.1 ^[37]
Lake water	Xi'an	1	1000	100	1.2	93.4±1.5	5.68±0.28	5.74±0.32
Ground water	Hancheng	1	5000	100	5	89.0±2.4	0.10±0.05	0.11±0.04 ^[20]
Rain	Xi'an	2	700-1500	100-300	10-12	91.7-99.5	-	_[19]
Ground water	Hancheng	2	5000	1000	> 20	92.0-99.9	-	_[20]

257 * Methods: 1. Rotary evaporation followed with solvent extraction;

258 2. Direct evaporation method using a hot plate below 100 °C.

259

260 **Conclusion**

261 In this study, the experimental conditions of water bath temperature, water sample pH
 262 and reductant addition are optimized in detail. The results show that when pH is 7,
 263 concentration of reducing agent is 5 mmol/L, water bath temperature is 60 °C, and final
 264 concentrated volume is 100 mL, the iodine recovery is as high as 99% for deionized
 265 water and slightly lower (> 93%) for real environmental water samples. This study also
 266 suggests that improper conditions of rotary evaporation will cause iodine loss of 5% or
 267 even up to 15%, which will underestimate ¹²⁹I concentration in environmental water
 268 samples. Compared with the traditional low-temperature evaporation method, the rotary
 269 evaporation method can effectively shorten the iodine pre-enrichment time by at least
 270 four times. Therefore, the rotary evaporation method is feasible and suitable for ¹²⁹I

271 analysis in large-volume environmental water samples, and this can serve to broaden ¹²⁹I
272 tracing applications in hydrogeological systems. Furthermore, this method can also be
273 used for reserving large-volume water samples in a smaller sample size.

274

275 **Author Information**

276 Corresponding author

277 Tel: 0086 029-62336195; Mobile: 0086 131 8601 7212; Email: zhangly@ieecas.cn;

278 houxl@ieecas.cn

279

280 **Acknowledgment**

281 Financial support from the National Natural Science Foundation of China (No. 11605207
282 and 91643206), the Technology Foundation for Selected Overseas Chinese Scholar,
283 Department of Human Resources and Social Security of Shaanxi Province, China, and
284 the Ministry of Science and Technology basic project (No. 2015FY110800) are gratefully
285 acknowledged.

286

287 **References**

- 288 1. Fabryka-Martin JT (1984) Natural Iodine-129 as a ground-water trace. The University
289 of Arizona
- 290 2. He P, Aldahan A, Possnert G, Hou XL (2013) A summary of global ¹²⁹I in marine
291 waters. Nucl Instrum Methods Phys Res Sect B 294:537-541

- 292 3. Hou XL, Hansen V, Aldahan A, Possnert G, Lind OC, Lujanienė G (2009) A review on
293 speciation of iodine-129 in the environmental and biological samples. *Anal Chim Acta*
294 632:181–196
- 295 4. Snyder G, Aldahan A, Possnert G (2010) Global distribution and long-term fate of
296 anthropogenic ^{129}I in marine and surface water reservoirs. *Geochem Geophys Geosyst*
297 11:1-19
- 298 5. Xing S, Hou XL, Aldahan A, Possnert G (2017) Speciation analysis of ^{129}I in seawater
299 using coprecipitation and accelerator mass spectrometry and its applications. *J Radioanal*
300 *Nucl Chem* 311:1-9
- 301 6. Xing S, Hou XL, Aldahan A, Possnert G, Shi KL, Yi P, Zhou WJ (2015) Iodine-129 in
302 snow and seawater in the Antarctica: Level and Source. *Environ Sci Technol* 49:6691-
303 6700
- 304 7. Raisbeck GM, Yiou F, Zhou ZQ, Kilius LR (1995) ^{129}I from nuclear fuel reprocessing
305 facilities at Sellafield (U.K.) and La Hague (France) potential as an oceanographic tracer.
306 *J Mar Syst* 6: 561-570
- 307 8. Hou XL (2004) Application of ^{129}I as an environmental tracer. *J Radioanal Nucl Chem*
308 262: 67-75
- 309 9. López-Gutiérrez JM, Santos FJ, García-León M, Schnabel C, Synal HA, Ernst T,
310 Szidat S (2004) Levels and temporal variability of ^{129}I concentrations and $^{129}\text{I}/^{127}\text{I}$
311 isotopic ratios in atmospheric samples from southern Spain. *Nucl Instrum Methods Phys*
312 *Res Sect B* 223-224:495-500

- 313 10. Snyder G, Fehn U (2004) Global distribution of ^{129}I in rivers and lakes: implications
314 for iodine cycling in surface reservoirs. Nucl Instrum Methods Phys Res Sect B 223–
315 224:579-586
- 316 11. Muramatsu Y, Yoshida S, Fehn U, Amachi S, Ohmomo Y (2004) Studies with
317 natural and anthropogenic iodine isotopes: iodine distribution and cycling in the global
318 environment. J Environ Radioact 74:221-232
- 319 12. Fehn U, Moran JE, Teng RTD, Rao U (1994) Dating and tracing of fluids using ^{129}I
320 and ^{36}Cl : results from geothermal fluids, oil field brines and formation waters. Nucl
321 Instrum Methods Phys Res Sect B 92:380–384
- 322 13. Fehn U, Snyder G, Egeberg PK (2000) Dating of pore waters with I-129: Relevance
323 for the origin of marine gas hydrates. Sci 289:2332-2335
- 324 14. Lu Z, Tomaru H, Fehn U (2008) Iodine ages of pore waters at Hydrate Ridge (ODP
325 Leg 204), Cascadia Margin: Implications for sources of methane in gas hydrates. Earth
326 Planet Sci Lett 267: 654-665
- 327 15. Moran JE, Fehn U, Hanor JS (1995) Determination of source ages and migration
328 patterns of brines from the U.S. Gulf Coast basin using ^{129}I . Geochim Cosmochim Acta
329 59: 5055-5069
- 330 16. Fabryka-Martin J, Bentley H, Elmore D, Airey PL (1985) Natural iodine-129 as an
331 environmental tracer. Geochim Cosmochim Acta 49:337-347
- 332 17. Hou XL, Zhou WJ, Chen N, Zhang LY, Liu Q, Luo MY, Fan YK, Liang W, Fu YC
333 (2010) Determination of ultralow level $^{129}\text{I}/^{127}\text{I}$ in natural samples by separation of
334 microgram carrier free iodine and accelerator mass spectrometry detection. Anal Chem
335 82:7713-7721

- 336 18. Park SD, Kim JS, Han SH, Ha YK, Song KS, Jee KY (2009) The measurement of ^{129}I
337 for the cement and the paraffin solidified low and intermediate level wastes (LILWs),
338 spent resin or evaporated bottom from the pressurized water reactor (PWR) nuclear
339 power plants. *Appl Radiat Isot* 67:1676-1682
- 340 19. Chen N, Zhou WJ, Hou XL, Fan YK, Xian F, Zhang LY, Liu Q, Jiang XH (2017)
341 Level and characteristic of ^{129}I of rain samples in Xi'an region, China. *J Earth Environ*
342 8:327-339
- 343 20. Ma XZ, Song Y, Liu SB, Jiang L, Hong F (2013) Origin and evolution of waters in
344 the Hancheng coal seams, the Ordos Basin, as revealed from water chemistry and isotope
345 (H, O, ^{129}I) analyses. *Sci China Earth Sci* 56:962-1970
- 346 21. Schwehr KA, Santschi PH, Moran JE, Elmore D (2005) Near-conservative behavior
347 of I in the orange county aquifer system, California. *Appl Geochem* 20:1461-1472
- 348 22. Moran JE, Oktay SD, Santschi PH (2002) Sources of iodine and iodine-129 in rivers.
349 *Water Resour Res* 38:24-1–24-10
- 350 23. Moran JE, Schink DR, Oktay S, Santschi PH (1999) Atmospheric dispersal of 129-
351 iodine from nuclear fuel reprocessing facilities. *Environ Sci Technol* 33:2536-2542
- 352 24. Dang HJ, Hou XL, Roos P, Nielsen SP (2013) Release of iodine from organic matter
353 in natural water by $\text{K}_2\text{S}_2\text{O}_8$ oxidation for ^{129}I determination. *Anal Methods* 5:449-456
- 354 25. Greene CR, Steinle SE (1959) Conversion of hydrogen iodide to iodine. US
- 355 26. Zhang LY, Hou XL, Xu S (2015) Speciation Analysis of ^{129}I and ^{127}I in Aerosols
356 Using Sequential Extraction and Mass Spectrometry Detection. *Anal Chem* 87:6937-
357 6944
- 358 27. Paparatto G, Gregorio G (1989) Process for the manufacture of iodine. US

- 359 28. Zhu HL, Liu LL (2004) Effect of temperature on iodine content in iodized salt.
360 Practical Medical Technology Magazine 11:2054-2054
- 361 29. Powers D (2000) Insight into the Control of the Release of Iodine, Cesium, Strontium,
362 and Other Fission Products in the Containment by Severe Accident Management.
363 NEA/CSNI/R 9:43-75
- 364 30. Zhang WN (2012) Studies on Speciation and Influencing Factors of Iodine in
365 Environment Water System. Jilin University
- 366 31. Younus I, Yim MS (2015) Out-containment mitigation of gaseous iodine by alkaline
367 spray in severe accident situation. Prog Nucl 83:167-176
- 368 32. Luo XZ (1986) A method for monitoring the course of oxidation of iodine ion during
369 radioactive iodination operation. At Energy Sci Technol 20:320-320
- 370 33. Liu Y, Hans R (1988) Migration chemistry and behaviour of iodine relevant to
371 geological disposal of radioactive wastes. PSI
- 372 34. Liang J, Jiang T, Wei SQ (2015) Absorption and Fluorescence Characteristics of
373 Dissolved Organic Matter (DOM) in Rainwater and Sources Analysis in Summer and
374 Winter Season. Environ Sci 3:888-897
- 375 35. Zhang LY, Zhou WJ, Hou XL, Chen N, Liu Q, He C, Fan YK, Luo MY, Wang Z, Fu
376 YC (2011) Level and source of ^{129}I of environmental samples in Xi'an region, China. Sci
377 Total Environ 409: 3780-3788
- 378 36. Fan YK, Hou XL, Zhou WJ (2013) Progress on ^{129}I analysis and its application in
379 environmental and geological researches. Desalination 321:32-46
- 380 37. Jiang XH (2017) Study on the Level of Change and Tracing of ^{129}I in Precipitation in
381 Xi'an Area. Chinese Academy of Sciences University

