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1 **Determination of ^{129}I in Environmental Solid Samples Using**
2 **Pyrolysis Separation and Accelerator Mass Spectrometry**
3 **Measurement**

4
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11

12 **Abstract:**

13 Due to high volatility and active chemical property of iodine, anthropogenic ^{129}I
14 released from human nuclear activities can be used as unique tracer for assessment of
15 nuclear environment safety and investigation of environmental process. For this
16 purpose, a reliable and sensitive analytical method for the determination of ^{129}I in
17 environmental samples is required. In this work, a pyrolysis method was proposed for
18 release of iodine from environmental solid samples. All parameters influencing the
19 releases of iodine including temperature, combustion duration, flow gases and rate,
20 iodine species were investigated, and mechanism of iodine released in pyrolysis was
21 explored. An optimal condition was proposed for quantitative separation of iodine from
22 environmental solid samples. The released iodine was trapped in alkali solution and
23 further separated using a simple and reliable AgI precipitation method. The separated
24 AgI was directly used for determination of ^{129}I using accelerator mass spectrometry
25 (AMS). The analytical quality of the method was validated by analysis of certified

reference materials of soil and sediment. Surface soil samples collected from the Northwest China were analyzed for ^{129}I , the results show that ^{129}I level in this area is significantly lower than that in the Europe and nuclear accident contaminated area, falling to the background level of North Hemisphere.

Keywords: iodine-129, environmental sample, soil, sediment, combustion, accelerator mass spectrometry

Introduction

Iodine-129, a long-lived (15.7 Ma) radionuclides, is naturally produced by cosmic ray reaction with Xe in the atmosphere and spontaneous fission of ^{238}U and neutron induced fission of ^{235}U in the earth, with minor contribution of neutron activation of tellurium on the earth, causing a nature $^{129}\text{I}/^{127}\text{I}$ ratio of 1.5×10^{-12} in the pre-nuclear samples [1, 2]. The natural occurred ^{129}I has been applied for age dating of geological events of 2-80 Ma [3]. ^{129}I is also a fission product of ^{238}U and ^{239}Pu , human nuclear activities have produced huge amount of ^{129}I , some of them have been released to the environment during nuclear weapons tests, nuclear accident and reprocessing of spent nuclear fuel, which increased the $^{129}\text{I}/^{127}\text{I}$ atomic ratio to $>10^{-10}$ [4]. Due to its high volatility and active chemical property, anthropogenic ^{129}I widely spreads in the environment with other radioisotopes of iodine through atmospheric dispersion [4], it can be used as tracer to investigate the environmental process and monitoring of nuclear environment safety [5-10]. Radioactive isotopes of iodine, especially short-lived radioiodine such as ^{131}I , are highly radiological toxic because of their high releases in the nuclear accident. Due to the same production model, the same chemical properties and environmental behaviors, ^{129}I can be used to reconstruct the level and distribution of short-lived radioiodine released from the nuclear accident after the short-lived radioiodine quickly disappeared by radioactive decay [11-13]. For these purposes, sensitive and accurate determination of ^{129}I in various environmental samples is required, among them,

53 environmental solid samples, such as soil, sediment and rock are most important
54 materials in these investigations.

55 ^{129}I is a beta decay radionuclide with emission of low energy gamma rays of low
56 intensity. Although radiometric methods such as gamma spectrometry and beta
57 counting can be used for its measurement, the low specific activity and ultra-low
58 concentration of ^{129}I in the environment make the determination of ^{129}I in normal
59 environmental samples using these techniques impossible [4]. Although ICP-MS has
60 also been proposed for measurement of ^{129}I , the low ionization efficiency of iodine and
61 serious isobaric interference of ^{129}Xe make it only possible to measure ^{129}I in nuclear
62 waste or contaminated environmental samples with $^{129}\text{I}/^{127}\text{I}$ ratio higher than 10^{-8} [14].
63 Accelerator mass spectrometry (AMS) and radiochemical neutron activation analysis
64 (RNAA) are the techniques for its determination in present environmental samples, and
65 AMS is the only method for determination of ^{129}I in samples with $^{129}\text{I}/^{127}\text{I}$ lower than
66 10^{-10} [4, 15-17]. Due to the limited sensitivity of RNAA, a large sample size (>20 soil
67 or >50 L seawater of background samples) is normally needed for accurate
68 determination of ^{129}I . Due to decreased number of nuclear research reactors assessable
69 for RNAA, it become less popular for the determination of ^{129}I in the past 10 years.

70 For determination of trace amount of ^{129}I in environmental samples, iodine has to be
71 separated from the sample matrix and interferences and prepared into a suitable form
72 for ^{129}I measurement. Due to the active chemical properties and complicated behavior
73 of iodine, ^{129}I is easy to be lost during chemical separation and sample preparation.
74 Effective separation of iodine from sample is a key issue for accurate determination of
75 low-level ^{129}I in environmental samples. A number of methods such as alkali fusion
76 [16], alkali leaching [18], acid digestion [19] and combustion [15, 11, 12, 20] can be
77 used to release iodine from the matrix of environmental solid samples and convert it
78 into an aqueous solution. Among these sample, acid digestion and alkali leaching
79 cannot completely release iodine from the sample matrix, because it does not
80 completely decompose sample, causing iodine associated with mineral crystals

remaining in the sample residues, causing an unreliable analytical results for some samples. Alkali fusion can completely decompose the sample, but introducing a large amount of chemicals, causing a high reagent blank and a low recovery of iodine.

Based on high volatility of iodine, pyrolysis/combustion method has been reported for separation of iodine from environmental solid samples [15], and different pyrolysis system have been established in different laboratories for this purpose [11, 12, 15, 20-24]. However, the reported pyrolysis methods and procedures vary from different lab, and the reported release efficiency of iodine in the pyrolysis procedures also vary, the behavior of different species of iodine in the pyrolysis process is not well investigated, and the effect of various parameters in the releases of iodine during pyrolysis are not completely understood. All these issues make the separation efficiency of iodine from different sample matrix not stable, influencing reliability of the final analytical results.

The released iodine in aqueous solution needs to be further purified and prepared to a suitable form for ^{129}I measurement. Solvent extraction following an AgI precipitation is the often used method for preparation of AgI target for AMS measurement of ^{129}I . This procedure is time consuming and produces large amount of toxic solvent (CHCl_3 or CCl_4) waste.

This work aims to develop a simple, reliable and sensitive method for determination of low-level ^{129}I in environmental solid samples by investigation of all parameters which might affect the release of iodine from environmental solid samples during pyrolysis process and well understanding the behaviors of iodine species in the pyrolysis process. A simple and effective method for iodine purification and target preparation is also established for AMS measurement of ^{129}I .

Experimental

Instrument and chemical reagents

107 A pyrolysis system (Pyrolyser-4 Trio TM, Raddec Inc. UK) was applied for separation
108 of iodine from solid environmental samples. The system (Fig. 1) consists of 4 quartz
109 tubes which were placed in a tube furnace. The whole furnace divided into three zones,
110 and the temperature of the sample and second zones can be controlled and programmed,
111 respectively. A NaI gamma detector (Xi'an Nuclear instrument Company, China) was
112 used to measure ¹²⁵I for chemical yield monitoring. The sample solution containing ¹²⁵I
113 tracer (1-3 ml) and ¹²⁵I standard (with the same volume as sample) were transferred to
114 a counting tube (5 ml) for counting ¹²⁵I.

115 ¹²⁹I standard solution (NIST-SRM-4949c) was purchased from the National Institute
116 Standard and Technology (Gaithersburg, MD), ¹²⁷I carrier solution with ultra-low ¹²⁹I
117 level (¹²⁹I/¹²⁷I atomic ratio <2×10⁻¹⁴) was prepared by dissolution of iodine crystal
118 (Woodward iodine, Woodward Iodine Corporation, Oklahoma, U.S.A.) into 0.40 mol/L
119 NaOH-0.05 mol/L NaHSO₃ solution. All chemical reagents used were of analytical
120 grade, and all solutions were prepared using deionized water (18.2 MΩ·cm).

121 ¹²⁵I (in NaI form, no reductant) was purchased from PerkinElmer Inc. (USA). ¹²⁵IO₃⁻
122 and ¹²⁵I labeled humic acid were prepared using ¹²⁵I⁻ solution.

123 For preparation of ¹²⁵IO₃⁻ solution, 200 kBq of ¹²⁵I (NaI) solution was taken to a beaker,
124 0.2 ml of 10% NaClO solution was added to oxidize ¹²⁵I⁻ to ¹²⁵IO₃⁻, the solution was
125 heated to dryness on a hotplate at 120°C to remove most of NaClO. 1.0 ml of water was
126 added to dissolve the residue, and the solution was loaded to an anion exchange column
127 (AG1-×4, Cl⁻ form, 2ml, Bio-Rad Laboratory, CA, USA), 2 ml of H₂O was added to
128 rinse the column. ¹²⁵I⁻ was removed by adsorption on the column, ¹²⁵IO₃⁻ in the effluent
129 and wash was collected and used as ¹²⁵IO₃⁻ tracer solution.

130 For preparation of ¹²⁵I labeled humic substances, 200 humic acid (Alfa Aesar, Thermo
131 fisher GmbH, Germany) was first dissolved in 0.01 mol/l NaOH solution. 1.0 ml of
132 humic acid solution and 500 kBq of ¹²⁵I⁻ (0.1 ml) was added to an Iodo-Gen tube (Pierce
133 iodination tube, Thermo Fisher Scientific Inc.) for iodine labeling at room temperature

for 15 min, after which the solution was removed from the reaction tube. The labeled humic acid was separated from free iodine and other chemical reagents using gel chromatography (a PD-10 desalting column, Amersham Bioscience, UK) by collecting the fraction of humic acid (the first peak).

Sampling and pretreatment of samples

Eight surface soil samples (0-10 cm) were collected in the Northwestern of China in July 2014 (Fig. 2) for investigation of ^{129}I level and distribution in Northwest China. One surface soil sample (0-10 cm) collected in Xi'an, China was used for method development. A lake sediment sample was collected in a small lake in Xi'an region in August 2015. A rock (sedimentary rock) sample was collected in Nantian, Shaanxi, China in 2015. The soil samples were first air-dried, and the stones and debris such as vegetation roots were removed. The samples were then dried in an oven at 70°C to constant weight (about 48 hours). The sediment sample was freeze dried and big debris (>3 mm) was removed. The dried soil and rock samples were ground and sieve through 200-mesh sieve for analysis. Two certified reference materials, soil (IAEA-375) and sediment (NIST-4354) were analysis for validation of the analytical method. The certified samples were dried at 70°C for overnight before analysis.

Separation of iodine from environmental solid samples by pyrolysis

The dried environmental solid samples (soil, sediment, rock, etc.) of up to 20 g was weighed in a quartz boat, ^{125}I tracer solution (200 Bq, in different species, iodide, iodate or ^{125}I labeled humic acid) was spiked to the sample. The sample boat was placed in the sample zone in the furnace tubes of the pyrolysis system. A U-type bubbler containing 35 ml of trapping solution (0.5 mol/l NaOH-0.02 mol/L NaHSO_3) was attached to the outlet of combustion tube with ground mouths. The flow rate of input gases (N_2+O_2 before 400°C and O_2 after 400°C) was adjusted to a certain value (50-550 ml/min). The

161 second heating zone was directly heated to 800°C within 30 min. The ramp procedure
162 of the first heating zone was programmed. The mid-zone heating was turn on when the
163 temperature of the sample zone was increased to be higher than 400 °C to ensure a
164 precise controlled temperature in the sample zone.

165 After combustion or at different time interval, the trap solution was transferred to a
166 centrifuge tube, the bubbler was washed 3 times with 6 ml water, and the wash solution
167 is combined to trap solution. 3.0 ml trap solution was taken to a counting tube for ^{125}I
168 measurement using the NaI gamma detector for monitoring the recovery of iodine. This
169 solution was returned to the original solution after gamma measurement. 1.0 ml trap
170 solution was taken for ^{127}I measurement using ICP-MS. The remained solution was
171 used for further separation of iodine for ^{129}I measurement.

172

173 **Separation of iodine from trap solution for target preparation**

174 Iodine trapped in the NaOH solution was further separated to prepare it as AgI
175 precipitate for AMS measurement of ^{129}I . 1.0 mg of ^{127}I carrier (with a $^{129}\text{I}/^{127}\text{I}$ ratio of
176 $< 2 \times 10^{-14}$) and 0.5 ml of 1.0 mol/l NaHSO_3 solution were added to the trap solution,
177 3.0 mol/l HNO_3 solution was then added to adjust pH1-2 to reduce iodate to iodide. 0.5
178 ml of 1.0 mol/l AgNO_3 solution was added to the sample solution, the formed AgI
179 precipitate was separated by centrifuge at 3000 rpm for 5 min. 5 ml of 3 mol/l HNO_3
180 was added to dissolve the formed Ag_2SO_3 and Ag_2SO_4 , and the AgI precipitate
181 remained in the centrifuge tube was separated by centrifuge. The precipitate was further
182 washed with 10 ml water to remove the remaining acid. After centrifuge, the AgI
183 precipitate was transferred to a 1.5 ml centrifuge tube using water, and then separated
184 by centrifuge. The precipitate (AgI) in the 1.5 ml centrifuge tube was finally dried at
185 60-70°C (2-3 hours).

186 Two ^{129}I standards with $^{129}\text{I}/^{127}\text{I}$ atomic ratios of $(1.01 \pm 0.03) \times 10^{-11}$ and (1.07 ± 0.03)
187 $\times 10^{-10}$ for AMS measurement of ^{129}I were prepared using a diluted ^{129}I standard solution

(NIST-SRM-4949c) and ^{127}I carrier (with $^{129}\text{I}/^{127}\text{I}$ ratio of $< 2 \times 10^{-14}$) by directly AgI precipitation as for the samples. Procedure blanks were prepared using the same method as samples using pyrolysis and AgI precipitation, which was performed in the same batch with sample analysis. In this case, the combusted soil sample was used as blank sample.

Measurement of ^{129}I by AMS

The dried AgI of samples, standard and procedure blanks in 1.5 ml centrifuge tube were ground to a fine powder and mixed with five times by mass of niobium powder (325-mesh, Alfa Aesar, Ward Hill, MA), which was finally pressed into a copper holder using a pneumatic press (Zhenjiang Aode Presser Instruments Ltd.). $^{129}\text{I}/^{127}\text{I}$ atomic ratios in the prepared targets were measured by AMS using 3MV Tandem AMS system (HVEE) in the Xi'an AMS center. I^{5+} ions was chosen for the measurement, where $^{127}\text{I}^{5+}$ was measured as charges (current) using a Faraday cup and $^{129}\text{I}^{5+}$ was measured using a gas ionization detector. All samples were measured for 6 cycles and 5 min per sample in each cycle. A detailed description of AMS system and measurement of ^{129}I has been reported elsewhere [17]. $^{129}\text{I}/^{127}\text{I}$ atomic ratios in procedure blanks were measured to be $< 2 \times 10^{-13}$, which is two orders of magnitude lower than that in the samples ($> 1 \times 10^{-11}$). The $^{129}\text{I}/^{127}\text{I}$ ratios in all samples were corrected for procedure blank and calibrated using the ^{129}I standards.

ICP-MS measurement of ^{127}I

Stable iodine (^{127}I) in the trap solution was measured using ICP-MS. 1.0 ml trap solution was taken and deionized using water for 20-200 times depending on the concentration of iodine in the sample. For 20 g rock, 5 g soil and 1 g sediment sample, the trap solution was diluted 100 times to get a iodine concentration of 0.5-10 ng/ml. Cs^+ solution (CsNO_3) was spiked to the diluted trap solution to a Cs concentration of 2 ng/ml. ^{127}I in the prepared samples was measured using ICP-MS (Agilent 8800). 1%

215 NH_3 solution was used as rinsing solution between samples. The detection limit of 0.01
216 ng/ml for ^{127}I was obtained (calculated as 3 times of blank). Iodine concentration in the
217 sample was calculated by correction for chemical yield in pyrolysis separation.

218

219 **3. Results and discussion**

220 In this work, iodine in the environmental solid samples was released by combustion at
221 high temperature in the present of oxygen using a tube furnace, and the released iodine
222 was trapped in a solution using a bubbler for further separation and measurement of ^{129}I
223 using AMS and ^{127}I using ICP-MS. It was observed that 30-100% of iodine was released
224 from the samples and collected in the trap solution depending on the temperature and
225 time duration of combustion, flow gases and their flow rates, the organic matters content
226 in the samples, size of samples, as well as the composition of the trap solution. All these
227 parameters were investigated enable to obtain an optimal method for effective
228 separation of iodine from the samples.

229 Iodine-125 (NaI) as a tracer was spiked to the sample before separation in the method
230 development. The behavior of $^{125}\text{I}^-$ in the combustion and solution trapping was
231 compared with other species of iodine.

232

233 **3.1 Effect of organic content and combustion procedure on the combustion of** 234 **solid samples**

235 The organic contents in the soil and sediment vary from 1% to more than 50% by weight.
236 It have been reported that an explosion might happened when the temperature was
237 quickly increased to 280-350 °C in combustion of vegetation samples [24], a similar
238 phenomenon was also reported in the combustion of high organic soil and sediment
239 samples [20]. This was attributed to the sudden ignition of organic substance in the tube
240 furnace and production of large amount of combustion gas (CO_2 , CO_2 , etc.), causing

dramatically buildup of high pressure in the combustion tube. In the combustion of a sediment sample with organic content of about 20%, it was also observed that the trap solution was flashed out when the temperature was quickly increased to about 350°C, followed by a suction of trap solution to the furnace tube, causing a damage of the qautz furnace tube. To avoid such an accident, a slow ignition was applied by increasing the temperature in a slow rate ($< 2^{\circ}\text{C}/\text{min}$) between 250-400 °C. Meanwhile, a mixed gas of O_2/N_2 (1:2) was flowed during the stage of ignition to reduce the ignition speed. Compressed air was not applied to reduce the ^{129}I blank contributed from the ^{129}I in the air, especially for the analysis of low-level ^{129}I samples. Therefore, in the combustion of solid samples, the temperature was first increased from room temperature to 250 °C in 20 minutes and remained at this temperature for 20 minutes to completely remove water/moisture from the sample (^{125}I tracer solution was spiked), which can also avoid the problem of splash of sample out of the sample boat during combustion. Afterward, the temperature was gradually increased to 400°C at a rate of $2^{\circ}\text{C}/\text{min}$ and remained for 30 minutes to carbonize all organic substance in the sample (Fig. 3).

256

3.2 Effect of temperature and time duration on release of iodine from soil/sediment during combustion

The temperature and time duration are key parameters to the release efficiency of iodine from solid samples during combustion. A combustion temperature of up to 1000 °C has been reported in the separation of iodine from soil samples [15, 21] and 900 °C for vegetation samples [20, 24]. Our results (Fig. 4) show that iodine start to be released from soil at 600°C, but only less than 55% iodine was released, extending combustion time could not significant increase the recovery of iodine after 3 hours. Increasing the combustion temperature can increase the recovery of iodine, 70% iodine was released at 700°C after 3 hours combustion. When the temperature was increased to $\geq 800^{\circ}\text{C}$, iodine can be quantitatively released. At 800°C, more than 96% iodine was released after one hour combustion, extending the combustion time can slightly improve the

269 recovery, but the differences are not significant under the analytical uncertainty.
270 Although the releases rate of iodine was improved from 68% to 82% in half hour
271 combustion at 900°C compared to 800 °C, but no significantly difference of iodine
272 release was measured after one hour combustion. At both temperature, iodine can be
273 quantitatively recovered (>96%) after one hour combustion. This is different to that
274 observed in the biological samples [24] that the recovery of iodine is less than 85%
275 even at 900 °C. The high recovery of iodine in the soil and sediment samples might
276 attributed to the less organic substances in this type of samples compared to vegetation.

277 In the RADDEC Pyrolyser system, there are three heating zones, the sample in quartz
278 boat was put in the first zone with an independent furnace. The temperatures for
279 carbonization and combustion discussed above are related to the temperature in the first
280 zone. The temperature in the second zone (outlet direction) was increased to 800°C
281 within 30 minutes after starting the experiment, i.e. before the temperature was
282 increased over 100 °C. Any organic species of iodine or sample particles escaped from
283 the sample boat at the first zone was decomposed to convert all iodine to gas inorganic
284 form (I_2 /HI/HIO, etc.) in the second zone of the furnace, which was trapped in the trap
285 solution in the bubbler. Between the sample zone and second zone, there is a mid-zone,
286 which acts as buffer to avoid the heating of the sample zone by the furnace in the second
287 zone, and precisely control the temperature. However, when the temperature in both
288 sample zone and second zone are increased to more than 800 °C, the second zone might
289 be at a lower temperature compared to both sample and second zone. Therefore, the
290 furnace in the mid-zone was turn on when the temperature of the sample zone increased
291 to more than 400°C (after carbonization of organic substances in the sample) to ensure
292 no condense and deposition of iodine in the working tube.

293 Based on these results, an optimal protocol for temperature control in the sample zone
294 of the combustion system is presented in Fig. 3. This protocol was programmed for the
295 first furnace in the sample zone in this system. The temperature in the third zone is set
296 to 800 °C, the temperature is directly increased to 800 °C within 30 minutes after the

power of the combustion system is turn on. The middle zone is set to off before the temperature of the sample zone is increased to 400 °C, and tune on afterwards. Meanwhile, the flow gas is changed to O₂ from the mixture of N₂ and O₂ when the temperature of the sample zone reach to 400 °C.

There is a ventilation setup in RADDEC Pyrolyser system, which can rapidly cool down the temperature in the furnace down to <60 °C in about 30 minutes, enabling to change the samples for the next batch experiment. With this function, 8 samples in two batches can be treated each day using the RADDEC pyrolyser-4 system (with 4 parallel tubes).

3.3 Effect of flow rate of the N₂/O₂ gases on the recovery of iodine during combustion

The flow gases of N₂/O₂ were used to assist the conversion of iodine in the sample to gaseous forms and carry the formed gaseous iodine to trapped solution. The flow rate of the N₂/O₂ is another key parameter affecting the recovery of iodine. The flow rate of both gases (N₂ and O₂) can be adjusted in the RADDEC pyrolyser system. Using the optimal protocol of combustion (Fig. 3), the effect of the flow rate (for both mixed gases of N₂ and O₂ before 400 °C and O₂ at 400-800°C) on the recovery of iodine was investigated. The results (Fig. 5) show a relative low recovery of iodine at low (<100 ml/min) and high flow rate (> 400 ml/min) in the present setup of the combustion system, and the optimal flow rates are 150-350 ml/min. The trend observed in this work is similar as those reported [20], but the optimal range and level of recovery are different. This might be attributed to the different size and structure of the combustion system including the bubbler.

The recovery of iodine decreases with decreased flow rate from 150 ml/min to 50 ml/ml, and dropped to less than 75% when the flow rate is 50 ml/min. (Fig. 5). This should be attributed to the backflow of the released gaseous iodine which condensed on the

entrance part of working tube, where the temperature is lower than 200°C even when the temperature of the sample zone raised to 800°. This was confirmed by the observation of some condensed water occurred in the entrance part of the work tube when the flow rate is lower than 100 ml/min. The measurement of ^{125}I in the washing solution of the entrance part of the work tube with 0.40 mol/l NaOH after the experiment with a flow rate of 50 ml/min showed that about 25% of the spiked ^{125}I to the samples was found. This is because that when the flow rate of the gases is slow, a significant back pressure was built during the ignition of the organic substance in the sample at about 350 °C, which flow back the formed gas to the entrance direction and deposited on the wall of the entrance part outside the furnace, where a low temperature occurred. In addition, the low flow rate of the gases might not sufficient to transport the formed gaseous iodine through the tube to the trap solution because of the pressure in the trap solution. Therefore, a lowest gas flow of 150 ml/min is needed in this system. Deposition of iodine on the outlet part of the work tube might be also happened because of the low temperature in outlet part of the work tube located outside the furnace. To overcome this problem, the outlet part of work tube outside the furnace was wrapped using heating tape [20, 23]. In this work, the outlet part of the work tube was shortened to less than 2 cm by moving the work tube to entrance direction, the high temperature in the second zone (800°C) and the short outlet part prevent iodine deposition, and ensure the released iodine enter to the trap solution. This is confirmed by no measurable ^{125}I in the washing solution of the outlet part of the work tube after combustion at flow rate of less than 400 ml/min.

The low recovery was also occurred at high flow rate (> 400 ml/min.) (Fig. 5), indicating an insufficient trapping of iodine in the trap solution or loss of the trap solution. In the combustion system, a bubbler with sintered glass frits containing micropores was employed to improve the contact time of gaseous iodine with trap solution, and therefore to improve the trapping efficiency of iodine. However, at high flow rate, the contact time of gaseous iodine with trap solution was shortened, causing insufficient

conversion of gaseous iodine species to water soluble species, to be trapped in the solution. It has been reported that blowing the trap solution spiked with ^{125}I (NaI) does not cause any significant loss of iodine in the trap solution at high flow rate [20]. However, when a bubbler with micro-pores sintered glass frits was employed, a large amount of small bubbles were produced when the flow rate become high. It has been observed when the flow rate was higher than 550 ml/min, the produced bubbles can be flow out of the bubbler. Therefore, the loss of the trap solution at high flow rate might be another reason causing a low recovery of iodine. This has been confirmed by an experiment using two sequentially connected bubblers. It was observed that when the flow rate was higher than 400 ml/min, ^{125}I in the trap solution of the second bubbler becomes measurable. When the flow rate increased to 550 ml/min, about 20% of iodine was measured in the second bubbler. Therefore, the flow rate of the gases was controlled to be 200-400 ml/min in the experiment.

4.4 Effect of chemical species of iodine in samples on its release during combustion

In the environmental samples such as soil, sediment and rock, iodine presents in different species, besides a small fraction as soluble iodide and iodate, iodine also associated with organic matter (mainly humic substance), oxides and minerals [4, 13, 25, 26]. Therefore, it might be questionable to monitor the chemical recovery of iodine in the combustion of soil, rock and sediment samples using ^{125}I iodide tracer. A similar recovery of iodine was observed when ^{125}I labeled humic acid was spiked as tracer compared to ^{125}I iodide [20]. In this work, we investigated the behavior of iodide, iodate and organic associated iodine during the combustion by spiking iodide-125, iodate-125 and ^{125}I labeled humic acid as yield tracers. The results (Table 1) show that the recovery of ^{125}I are equally higher than 95% for three species of ^{125}I spikes for difference size of soil, sediment and rock samples (from 1g to 20 g) when the proposed combustion protocol was applied. This indicates the species of iodine does not have a significant

effect on the releases of iodine from these environmental samples. Since it is not easy to synthesize/label radioactive iodine to mineral and oxides, two standard reference materials IAEA-375 (soil) and NIST-5354 (lake sediment) were analyzed using the developed method. The results (Table 1) show that the measured concentration of ^{127}I and ^{129}I are in a good agreement to the reference values or literature values, indicating that all species of iodine in these environmental solid samples were released from the samples during the combustion and absorbed in the trap solution.

In the separation of iodine from solid sample using combustion, it was supposed that iodine was oxidized to molecular iodine (I_2) in oxygen atmosphere. To improve the recovery of iodine in the combustion, oxidant (V_2O_5) mixed with sample, oxygen atmosphere and high temperature up to $1000\text{ }^\circ\text{C}$ has been applied for separation of iodine in the combustion of environmental solid samples (e.g. soil) [15, 22, 27]. However, the iodate-125 spiked to the solid samples was also quantitatively collected in the trap solution during the combustion. Iodate is the highest oxidation state of iodine in the environment, which could not be convert to I_2 in an oxidizing atmosphere (O_2). The high recovery of iodate-125 during combustion might attributed to the low melting point of iodate ($560\text{ }^\circ\text{C}$), which might become volatile at high temperature, and released from the sample and finally collected in the trap solution, due to its high solubility in water. The iodine associated to oxides and mineral was also released during the combustion, it might be also attributed to its high migration of iodine atoms and high volatility of iodine in the high temperature even associated inside of the crystal of mineral and oxides. Our experiment on the releases of iodine-125 produced inside tungsten block by irradiation of high-energy proton during combustion at helium atmosphere confirmed that iodine can migrate from the metal crystal to the surface at high temperature. Iodine associated with organic substance is normally from C-I bond, which can be decomposed during combustion, meanwhile iodine is oxidized to I_2 in O_2 atmosphere or directly released as HI or HIO at high temperature. Since O_2 was applied and high iodine recovery in the combustion, no oxidant (e.g. V_2O_5) is needed to be

408 added to the sample, which also reduce the possible contamination of ^{129}I in the analysis
409 of low-level ^{129}I samples.

410

411 **3.5 Collection of iodine released from the sample during combustion**

412 In the combustion of sample, iodine was released as gaseous iodine, which has to be
413 collected and converted to suitable forms for measurement of iodine isotopes. Active
414 charcoal and alkali solution have been used for collected the released iodine [15, 21].

415 To improve the trapping efficiency of iodine, sulfite reductant (e.g. NaHSO_3) has been
416 added to the trap solution. Our results has showed a high recovery of iodine even using
417 only water without reductant (>65%). It is well known that molecular iodine (I_2) has
418 low solubility in water, and the solubility increased when iodide presents in the water
419 to form relative stable I_3^- species. Although a disproportionation reaction of I_2 in water
420 can happen for forming iodide and IO_3^- , but it is not favorite in neutron and acidic
421 medium. The relative high recovery of iodine in water during combustion (65%) might
422 indicate that the released iodine is not only in form of I_2 , but also other species such as
423 iodate (as discussed above), iodide (e.g. HI) and HIO , which are high water solubility.

424 It was also observed that the recovery of iodine was improved in alkali solution, the
425 recovery of iodine is higher than 93% when more than 0.1 mol/l NaOH was applied as
426 trap solution. This is attributed to the disproportionation reaction of I_2 in the alkaline
427 solution to form iodide and iodate. Further increasing the NaOH concentration to 0.4
428 mol/l NaOH can slightly improve the recovery to more than 95%. Reductant such as
429 Na_2SO_3 or NaHSO_3 has been added to the trap solution to improve the trapping
430 efficiency of iodine during the combustion [15]. This is based on the reduction of I_2 by
431 sulfite to more stable iodide, therefore improving the trapping efficiency. However, our
432 results do not show any significant improvement of recovery of iodine by addition of
433 NaHSO_3 solution in the combustion of soil and sediment sample. This might because
434 that the dominant process of iodine in the trap solution is dissolution of soluble iodide,

435 iodate and HIO and disproportionation of I_2 in alkaline solution. It has been observed
436 that sulfite can significantly improve the trapping efficiency of iodine in the combustion
437 of vegetation samples [24]. This was attributed to the elimination of oxidizing reagents
438 produced during combustion of vegetation, and sulfite can react with these oxidizing
439 reagents, consequently prevent the loss of iodine from the trap solution during
440 combustion.

441 In some sediment samples, organic substance might be high, a trap solution of 0.40
442 mol/l NaOH– 0.05 mol/l Na_2SO_3 was recommended as trap solution. However, a low
443 concentration NaOH (0.05 mol/l and Na_2SO_3 (<0.01 mol/l) should be used when low
444 iodine and organic substance samples (e.g rock) is analyzed, because the high
445 concentration of NaOH and Na_2SO_3 influence the measurement of ^{127}I using ICP-MS
446 due to matrix effect and high dilution needed.

447

448 **3.6 Separation and purification of iodine for AMS measurement of ^{129}I using AMS**

449 In the AMS measurement of ^{129}I , the separated iodine needs to be prepared to solid
450 form, mixed with conductive material and pressed into a target holder for ionizing to I^-
451 ion by bombardment using Cs^+ in the ion source chamber. Iodine in the trap solution is
452 often separated by solvent extraction using CCl_4 or $CHCl_3$, and then back-extracted to
453 aqueous phase as iodide, which is finally precipitated as AgI precipitate for AMS
454 measurement. CCl_4 and $CHCl_3$ are toxic organic solvent, a large volume of such toxic
455 waste will be produced when a large number of samples are analyzed. Iodine collected
456 in the trap solution present as inorganic iodine (iodide and iodate), a direct AgI
457 precipitation was applied to separate ^{129}I in the trap solution after reducing all iodine to
458 iodide using Na_2SO_3 at pH 1-2. Since iodine concentrations in the terrestrial samples
459 (soil, lake sediment and rock) are normally low (< 10 $\mu g/g$), the amount of iodine in the
460 trap solution is too small (< 1-100 μg) to be separated by AgI precipitation due to the
461 small mass, which is suspended in the solution in small particle to prevent to be

collected during centrifuge. Therefore iodine carrier with low ^{129}I level ($^{129}\text{I}/^{127}\text{I}$ ratio $< 2 \times 10^{-14}$) was added to the trap solution before precipitation, by this way, iodine in the trap solution can be well separated and prepared as AgI (recovery of iodine $> 90\%$). It should be mentioned, the trap solution has to be acidify to pH1-2 using HNO_3 and small amounts of Na_2SO_3 or NaHSO_3 solution should be added to ensure all iodine is converted to iodide. In addition, at acidic medium, the formed AgI particles can easily aggregate to form large particles for its separation by centrifuge. In addition, acidic condition can also significantly reduce the adsorption of AgI particles on the wall of the centrifuge tube and pipette, therefore improve the recovery of iodine in this step.

In some soil and marine sediment samples, high chlorine content might occur in the trap solution, because chlorine is also volatile at oxygen atmosphere and high temperature. Chloride in the trap solution is also precipitated as AgCl with AgI when AgNO_3 was added. The large amount of AgCl in the precipitate will dilute AgI in the target, consequently worsening the detection limit of ^{129}I . In this case, AgCl should be removed by washing the precipitate using 25% $\text{NH}_3 \text{ H}_2\text{O}$. By repeating washing process, more than 99% of AgCl can be eliminated.

For low ^{129}I level samples, addition of ^{127}I carrier might increase the background of ^{129}I . We have proposed a separation method of carrier free ^{129}I using AgI-AgCl precipitation [17], which has been successfully used for determination of ^{129}I in seawater and precipitation from the Antarctic [28, 29]. In the analysis of environmental solid samples, such as rock sample, small amount of chloride (0.5 mg) can be added to the trap solution, the formed AgI-AgCl co-precipitate is then separated by centrifuge after addition of sufficient amount of AgNO_3 . The separated AgI-AgCl is directly pressed into target holder after mixed with niobium powder for AMS measurement.

In the AMS measurement of ^{129}I , AgI precipitate is often mixed with niobium or silver power and pressed in a target holder made of aluminum, copper or stainless steel. A solid phase reaction of AgCl and aluminum has been reported when water vapor presence, which will convert the pressed AgCl to liquid form, all samples in the target

490 will be splashed to the ion source chamber when bombarding with Cs⁺ source,
491 consequentially contaminated the ion source, cause a serious cross contamination
492 during AMS measurement [30]. Therefore, target holder made of copper is always
493 applied for AMS measurement of ¹²⁹I, because chlorine is always present in
494 environmental samples in a large concentration compared to iodine, and some amount
495 of AgCl is often presented in the prepared AgI target.

496

497 **3.7 Detection of low-level ¹²⁹I in environmental samples**

498 AMS is a sensitive method for measurement of ¹²⁹I, a ¹²⁹I/¹²⁷I atomic ratio down to
499 2×10^{-14} was measured in ¹²⁷I carrier (Woodward Inc., USA), which was produced from
500 a deep brine (very old iodine water). This is corresponding to a ¹²⁹I level of 2×10^5 atoms
501 (4×10^{-17} g) considering about 2 mg iodine as AgI was pressed into the target. However,
502 a slight highly ¹²⁹I/¹²⁷I atomic ratio of 1.0×10^{-13} was measured in the procedure blank
503 of the proposed method when 1.0 mg of iodine carrier was added. Using a 3 time
504 procedure blank level, a detection limit of ¹²⁹I/¹²⁷I ratio of 3.0×10^{-13} can be calculated,
505 which corresponding to a detection limit of 1.4×10^6 atoms (0.3 fg).

506 The lowest ¹²⁹I level was measured in the rock sample (9.8×10^5 atoms/g) (Table 1), the
507 ¹²⁹I/¹²⁷I atomic ratio in the separated AgI target was measured to be 4.3×10^{-12} , which is
508 more than 40 times higher than that in the procedure blank. For such a low level
509 samples, the analytical results of ¹²⁹I has to be corrected by subtracting the procedure
510 blank.

511 Two certified reference materials, soil (IAEA-375) and sediment (NIST-4354) were
512 analyzed using the proposed method, the results (Table 1) show that the measured ¹²⁹I
513 concentration of $(12.6 \pm 0.7) \times 10^8$ atom/g in soil certified reference material (IAEA-375)
514 agrees well with the reference values of 12×10^8 atom/g. No ¹²⁹I value was certified in the
515 sediment NIST-4353, the measured ¹²⁹I concentration of $(324 \pm 12) \times 10^8$ atom/g agrees well
516 with the reported ¹²⁹I concentration of $(312 \pm 43) \times 10^8$ atom/g in the literature [25]. This

517 confirms the proposed method is reliable and accurate for the determination of ^{129}I in
518 environmental solid samples.

519

520 **3.8 Analysis ^{129}I and ^{127}I in soil samples collected in Northwestern China**

521 ^{129}I and ^{127}I concentrations in 8 surface soil samples collected from Northwest China
522 (Fig. 1) were determined using the proposed method. The recovery of iodine in the
523 combustion monitored by the spiked ^{125}I are more than 97%. This confirmed that the
524 developed method could be well used for analyzed different types of soil with a
525 quantitative separation of iodine. The overall recovery of iodine including the step of
526 AgI precipitation are more than 90%, indicating a satisfactory separation of iodine of
527 iodine in overall procedure.

528 The analytical results (Table 2) show a large variation of ^{129}I and ^{127}I concentrations
529 and $^{129}\text{I}/^{127}\text{I}$ ratios in these surface soil samples. The concentrations of ^{127}I range from
530 0.43 to 13.47 $\mu\text{g/g}$, this might be attributed to the different types of soil. The low iodine
531 concentration was observed in the sandy soil which was collected in the Gobi area in
532 the Northwest China, which contains a high sand and less organic substance (ignition
533 loss of less than 2%). The measured ^{129}I concentrations range from 5.9×10^6 to 257×10^6
534 atoms/g, the high variation of ^{129}I in the surface soil should be attributed to the different
535 sample type and different sources of ^{129}I . The measured $^{129}\text{I}/^{127}\text{I}$ atomic ratios are $(0.53-$
536 $10.4) \times 10^{-9}$, which is comparable to the ratios in surface soil observed in Xi'an region
537 $(0.1-4.4) \times 10^{-9}$ [32] and background region of Japan (no direct contamination by nuclear
538 facilities) in Japan. However, the measured $^{129}\text{I}/^{127}\text{I}$ ratios are significantly higher than
539 those measured in the surface soil collected in Chili (10^{-12} - 10^{-10}) [33], this agrees with
540 the low fallout level of radioactivity in the south hemisphere, because most of nuclear
541 weapons tests were carried out in the North Hemisphere. In addition, the ^{129}I released
542 from the reprocessing plants at Sellafield (UK), La Hague (France) and others locations
543 was also mainly deposited in the North Hemisphere, causing a high ^{129}I level in the

544 North Hemisphere compared to the South Hemisphere [28, 29]. High $^{129}\text{I}/^{127}\text{I}$ ratios up
545 to 10^{-8} - 10^{-6} have been observed in the soil collected from Denmark [16], Germany [21,
546 33] and Slovenia [31] in the Europe, this is mainly attributed to the highly releases of
547 two European reprocessing plants. The highest $^{129}\text{I}/^{127}\text{I}$ ratios of 10^{-7} - 10^{-5} in the nuclear
548 accident contaminated soils such as in the Chernobyl and Fukushima accident highly
549 contaminated soil samples [11-13, 31, 34]. This indicates that the ^{129}I level in these soil
550 samples from the Northwest China fall into the background level of ^{129}I in the North
551 Hemisphere, it mainly originated from the global fallout of nuclear weapons tests and
552 large-distance dispersion of reprocessing released ^{129}I .

553

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569 **References**

- 570 1. Fabryka-Martin J, Bentley H, Elmore D, Airey PL (1985) Natural iodine-129 as
571 an environmental tracer. *Geochim Cosmochim Acta* 49: 337-347
- 572 2. Moran JE, Fehn U, Teng RTD (1998) Variations in $^{129}\text{I}/^{127}\text{I}$ ratios in recent marine
573 sediments, evidence for a fossil organic component. *Chem Geol* 152:193-203
- 574 3. Fehn U, Snyder G, Egeberg PK (2000) Dating of pore water with ^{129}I relevance
575 for the origin of marine gas hydrates. *Science* 289:2332-2335
- 576 4. Hou XL, Hansen V, Aldahan A, Possnert G, Lind OC, Lujaniene G (2009) A
577 review on speciation of iodine-129 in the environmental and biological samples.
578 *Anal Chim Acta* 632:181–196
- 579 5. Snyder, G., A. Aldahan, G. Possnert (2010). Global distribution and long-term
580 fate of anthropogenic ^{129}I in marine and surface water reservoirs. *Geochem*
581 *Geophys Geosyst* 2010. **11**, Q04010, doi:10.1029/2009GC00210.
- 582 6. Hou X L, Aldahan A, Nielsen SP, Possnert G, Nies H, Hedfors J (2007)
583 Speciation of ^{129}I and ^{127}I in seawater and implications for sources and transport
584 pathways in the North Sea. *Environ Sci Technol* **41**(17):5993-5999
- 585 7. Raisbeck GM, Yiou F, Zhou ZQ (1995) ^{129}I from nuclear fuel reprocessing
586 facilities at Sellafield (U.K.) and La Hague (France); potential as an
587 oceanographic tracer. *J Mar Sys* **6**(5-6): 561-570
- 588 8. Reithmeier H, Lazarev V, Rühm W, Nolte E (2010). Anthropogenic ^{129}I in the
589 atmosphere: Overview over major sources, transport processes and deposition
590 pattern. *Sci Total Environ* **408**(21):5052-5064
- 591 9. Karcher M, Smith JN, Kauker F, Gerdes R, Smethie JWM (2012) J. Recent
592 changes in Arctic Ocean circulation revealed by iodine-129 observations and
593 modeling. *J Geophys Res* 117, C08007, doi:10.1029/2011JC007513
- 594 10. Hou XL, Povinec PP, Zhang LY, Shi KL, Biddulph D, Chang CC, Fan YK,
595 Golser R, Hou YK, Jeskovsky M, Jull AJT, Liu Q, Luo MY, Steier P, Zhou WJ

- (2013) Iodine-129 in Seawater Offshore Fukushima: Distribution, Inorganic Speciation, Sources, and Budget. *Environ Sci Technol* 47(7):3091-3098
11. Michel M., Daraoui A, Gorny M, Jakob D, Sachse R, Romantschuk LD, Alifimov V, Synal H-A (2015) Retrospective dosimetry of iodine-131 exposures using iodine-129 and caesium-137 inventories in soils – A critical evaluation of the consequences of the Chernobyl accident in parts of Northern Ukraine. *J Environ Radioact* 150:20-35
12. Muramatsu Y, Matsuzaki H, Toyama C, Ohno T (2015) Analysis of ^{129}I in the soil of Fukushima prefecture: preliminary reconstruction of ^{131}I deposition related to the accident at Fukushima Daiichi NPP. *J Environ Radioact* 139: 344-350
13. Hou XL, Fogh HC, Kucera J, Andersson KG, Dahlgard H, Nielsen SP (2003) Iodine-129 and Caesium-137 in Chernobyl contaminated soil and their chemical fractionation. *Sci Total Environ* 308(1-3):97-109
14. Ohno T, Muramatsu Y, Shikamori Y, Toyama C, Okabe N, Matsuzaki H (2013) Determination of ultratrace ^{129}I in soil samples by triple quadrupole ICP-MS and its application to Fukushima soil samples. *J Anal At Spectrom* 28:1283-1287
15. Muramatsu Y, Uchida S, Sumiya M, Ohmomo Y (1985) Iodine separation procedure for the determination of ^{129}I and ^{127}I in soil by neutron activation analysis, *J Radioanal Nucl Chem Lett* 94:329-338
16. Hou XL, Dahlgard H, Rietz B, Jacobensen U, Nielsen SP, Aarkrog A (1999) Determination of ^{129}I in seawater and some environmental materials by neutron activation analysis. *Analyst* 124:1109-1114
17. Hou XL, Zhou WJ, Chen N, Zhang LY, Liu Q, Luo MY, Fan YK, Liang WG, Fu YC (2010) Determination of Ultralow Level $^{129}\text{I}/^{127}\text{I}$ in Natural Samples by Separation of Microgram Carrier Free Iodine and Accelerator Mass Spectrometry Detection. *Anal Chem* 82(18):7713-7721
18. Yang GS, Tazoe H, Yamada M (2018) Improved approach for routine monitoring ^{129}I activity and $^{129}\text{I}/^{127}\text{I}$ atom ratio in environmental samples using TMAH extraction and ICP-MS/MS. *Anal Chim Acta* 1008:66-73

- 625 19. Gómez-Guzmán JM, Enamorado-Báez SM, Pinto-Gómez AR, Abril-Hernández
 626 JM (2011) Microwave-based digestion method for extraction of ^{127}I and ^{129}I from
 627 solid material for measurements by AMS and ICP-MS. *Intern J Mass Spectrom*
 628 303:103–108
- 629 20. Herod MN, Cornett RJ, Clark ID, Kieser WE, Jean GS (2014) Extraction of ^{129}I and
 630 ^{127}I via combustion from organic rich samples using ^{125}I as a quantitative tracer. *J*
 631 *Environ Radioact* 138:323-330
- 632 21. Aumann D.C., Güner D., Determination of ^{129}I in soil of Germany using
 633 radiochemical neutron activation analysis. *J. Radioanal. Nucl. Chem.* 1999, 242(3),
 634 641-645.
- 635 22. Matsuzaki H, Muramatsu Y, Kato K, Yasumoto M, Nakano C (2007)
 636 Development of ^{129}I -AMS system at MALT and measurement of ^{129}I
 637 concentration in several Japanese soils. *Nucl Instr Methods Phys Res B* 259:721-726
- 638 23. Englund E, Aldahan A, Possner G, Alfimov V (2007) A routine preparation
 639 method for AMS measurement of I-129 in solid material. *Nucl Instr Methods Phys*
 640 *Res B* 259:365-369
- 641 24. Hou XL, Wang YY (2006) Determination of ultra-low level ^{129}I in vegetation using
 642 pyrolysis for iodine separation and accelerator mass spectrometry measurement. *J*
 643 *Anal At. Spectrom* 31:1298-1310
- 644 25. Qiao JX, Hansen V, Hou XL, Aldahan A, Possner G (2012) Speciation analysis
 645 of ^{129}I , ^{137}Cs , ^{232}Th , ^{238}U , ^{239}Pu and ^{240}Pu in environmental soil and sediment.
 646 *Appl Radiat Iso* 70:1698-1708.
- 647 26. Luo MY, Hou XL, Zhou WJ, He CH, Chen N, Liu Q, Zhang LY (2013) Speciation
 648 and migration of ^{129}I in soil profiles. *J Environ Radioact* 118:30-39
- 649 27. Muramatsu Y, Takada Y, Matsuzaki H, Yoshida S (2008) AMS analysis of I-129
 650 in Japanese soil samples collected from background areas far from nuclear
 651 facilities. *Quat Geochronol* 3(3):291-297
- 652 28. Xing S, Hou XL, Aldahan A, Possner G, Shi KL, Yi P, Zhou WJ (2015). Iodine-
 653 ^{129}I in Snow and Seawater in the Antarctic: Level and Source. *Environ Sci Technol*

654 **49**(11): 6691-6700.

655 29. Xing S, Hou XL, Aldahan A, Possnert G, Shi KL, Yi P, Zhou WJ (2017) Water
656 circulation and marine environment in the Antarctic traced by speciation of ¹²⁹I
657 and ¹²⁷I. *Sci Rep* 7(1), 7726

658 30. Liu Q, Hou XL, Zhou WJ, Fu YC (2015) Accelerator mass spectrometry analysis
659 of ultra-low level ¹²⁹I in carrier-free AgI-AgCl sputter target. *J Am Soc Mass*
660 Spectrom 26(5):725-733

661 31. Osteric A, Stibilj V (2013) ¹²⁹I level in soil from Ukraine and Slovenia in the last
662 decade, *Intern J Environ Anal Chem* 93(5): 553-564.

663 32. Zhang LY, Zhou WJ, Hou XL, Chen N, Liu Q, He CH, Fan YK, Luo MY, Wang
664 ZW, Fu YC (2011) Level and source of ¹²⁹I of environmental samples in Xi'an
665 region, China. *Sci Total Environ* 409:3780-3788

666 33. Daraoui A, Michel R, Gorny M, Jakob D, Sachse R, Synal HA, Alfimov V (2012)
667 Iodine-129, Iodine-127 and Caesium-137 in the environment: soils from Germany
668 and Chile. *J Environ Radioactiv* 112:8-22.

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680 **Caption of figures:**

681

682 Fig. 1 a) Schematic diagram of the Pyrolyser-4 Trio TM system for separation of iodine
683 from solid samples; b) photo of the combustion system. The system consists of 4
684 parallel work tubes (quartz) and two furnaces in the sample zone and second zone,
685 respectively.

686 Fig. 2 Sampling locations of surface soil samples in Northwest China

687 Fig. 3 Protocol of the stepwise temperature control of Pyrolyser system for release of
688 iodine from environmental solid samples

689 Fig. 4 Effect of temperature and heating duration on the releases of iodine from soil
690 samples in the combustion

691 Fig. 5 Flow rate of gases (N₂/O₂) on the recovery of iodine in the combustion

692

Table 1 Separation of iodine in environmental solid samples by combustion

Conditions: combustion at 800 °C for 1 hour, 250 ml/min flow rate, 35 ml of 0.4 mol/l NaOH-0.05M NaHSO₃ trap solution.

Sample	Weight (g)	Spiked ¹²⁵ I tracer	Recovery of ¹²⁵ I (%)	Measured ¹²⁷ I, (μg/g)	Certified or literature value of ¹²⁷ I, (μg/g)	Measured ¹²⁹ I (×10 ⁸ atom/g)	Certified or literature value of ¹²⁹ I (×10 ⁸ atom/g)
Soil	5.0	¹²⁵ Iodide	96.4±2.6	2.15±0.16		1.26±0.09	
Soil	20.0	¹²⁵ Iodide	97.8±2.1	2.27±0.19		1.23±0.06	
Soil	5.0	¹²⁵ Iodate	95.8±3.1	2.09±0.08		1.24±0.10	
Soil	20.0	¹²⁵ Iodate	96.2±2.5	2.07±0.11		1.21±0.06	
Soil	5.0	¹²⁵ I-humic acid	96.2±2.0	2.11±0.11		1.28±0.09	
Soil	20.0	¹²⁵ I-humic acid	96.2±2.8	2.19±0.11		1.26±0.06	
Sediment	5.0	¹²⁵ Iodide	95.4±3.5	15.2±0.5		7.73±0.32	
Sediment	5.0	¹²⁵ Iodate	95.9±2.2	15.9±0.6		8.00±0.28	
Sediment	5.0	¹²⁵ I-humic acid	96.9±2.6	15.4±0.7		8.12±0.31	
Rock	20.0	¹²⁵ Iodide	97.4±3.0	0.560±0.022		(9.38±1.70)×10 ⁻³	
Rock	20.0	¹²⁵ Iodate	96.9±2.7	0.571±0.025		(10.7±1.6) ×10 ⁻³	
Soil (IAEA-375)	3.0	¹²⁵ Iodide	97.1±2.5	1.83±0.08	1.74±0.05 (2)	12.6±0.7	12 (1)
					1.85±0.77 (3)		
Sediment (NIST-4354)	1.0	¹²⁵ Iodide	97.1±2.5	7.43±0.31	7.08±0.57 (4)	324±12	312±43 (4)

(1) Certified/reference value of ¹²⁹I in soil reference material (IAEA-375);

(2, 3) Reported values of ¹²⁷I in literatures [31,20]

(4) Reported values of ¹²⁹I in literature [25]

Table 2 Analytical results of the concentrations of ^{127}I and ^{129}I in surface soil samples collected from Northwest China.

Sample Code	Sampling location	Latitude ° N	Longitude ° E	^{127}I conc. $\mu\text{g/g}$	^{129}I conc. $\times 10^6$ atoms/g	$^{129}\text{I}/^{127}\text{I}$ atoms ratio, $\times 10^{-9}$	Recovery of iodine in combustion	Total recovery of iodine
S01	Qingshuihe	37.36	105.62	0.43 ± 0.01	7.66 ± 0.15	3.78 ± 0.17	97.64%	95.86%
S02	Jiuduntown	38.18	102.76	1.07 ± 0.01	52.6 ± 0.4	10.4 ± 0.58	96.69%	86.23%
S03	Gangcha	37.27	100.31	13.5 ± 0.2	63.9 ± 0.5	1.00 ± 0.02	97.08%	94.26%
S04	Xiningdong	36.48	102.20	8.21 ± 0.06	41.6 ± 0.7	1.07 ± 0.02	97.86%	96.74%
S05	Jiejiazui	35.90	104.17	2.41 ± 0.03	48.1 ± 0.8	4.21 ± 0.10	97.24%	90.98%
S06	Hami	42.98	93.43	9.78 ± 0.36	257 ± 3	5.54 ± 0.21	99.50%	90.41%
S07	Weilinan	41.26	86.30	2.34 ± 0.04	5.89 ± 0.17	0.53 ± 0.03	97.96%	89.47%
S08	Yangtakelangan	39.79	88.38	1.30 ± 0.02	7.69 ± 0.16	1.25 ± 0.07	99.71%	90.92%

a)

b)

Fig. 1 a) Schematic diagram of the Pyrolyser-4 Trio TM system for separation of iodine from solid samples; b) photo of the combustion system. The system consists of 4 parallel work tubes (quartz) and two furnaces in the sample zone and second zone, respectively.

Fig. 2 Sampling locations of surface soil samples in Northwest China

Fig. 3 Protocol of the stepwise temperature control of Pyrolyser system for release of iodine from environmental solid samples

Fig. 4 Effect of temperature and heating duration on the releases of iodine from soil samples in the combustion

Fig. 5 Flow rate of gases (N₂/O₂) on the recovery of iodine in the combustion