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Determination of $^{129}$I in Environmental Solid Samples Using Pyrolysis Separation and Accelerator Mass Spectrometry Measurement

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Abstract:

Due to high volatility and active chemical property of iodine, anthropogenic $^{129}$I released from human nuclear activities can be used as unique tracer for assessment of nuclear environment safety and investigation of environmental process. For this purpose, a reliable and sensitive analytical method for the determination of $^{129}$I in environmental samples is required. In this work, a pyrolysis method was proposed for release of iodine from environmental solid samples. All parameters influencing the releases of iodine including temperature, combustion duration, flow gases and rate, iodine species were investigated, and mechanism of iodine released in pyrolysis was explored. An optimal condition was proposed for quantitative separation of iodine from environmental solid samples. The released iodine was trapped in alkali solution and further separated using a simple and reliable AgI precipitation method. The separated AgI was directly used for determination of $^{129}$I using accelerator mass spectrometry (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 $^{129}$I/$^{127}$I ratio of $1.5 \times 10^{-12}$ 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 $^{129}$I/$^{127}$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,
environmental solid samples, such as soil, sediment and rock are most important materials in these investigations.

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

For determination of trace amount of $^{129}$I in environmental samples, iodine has to be separated from the sample matrix and interferences and prepared into a suitable form for $^{129}$I measurement. Due to the active chemical properties and complicated behavior of iodine, $^{129}$I is easy to be lost during chemical separation and sample preparation. Effective separation of iodine from sample is a key issue for accurate determination of low-level $^{129}$I in environmental samples. A number of methods such as alkali fusion [16], alkali leaching [18], acid digestion [19] and combustion [15, 11, 12, 20] can be used to release iodine from the matrix of environmental solid samples and convert it into an aqueous solution. Among these sample, acid digestion and alkali leaching cannot completely release iodine from the sample matrix, because it does not 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**
A pyrolysis system (Pyrolyser-4 Trio™, Raddec Inc. UK) was applied for separation of iodine from solid environmental samples. The system (Fig. 1) consists of 4 quartz tubes which were placed in a tube furnace. The whole furnace divided into three zones, and the temperature of the sample and second zones can be controlled and programmed, respectively. A NaI gamma detector (Xi’an Nuclear instrument Company, China) was used to measure $^{125}\text{I}$ for chemical yield monitoring. The sample solution containing $^{125}\text{I}$ tracer (1-3 ml) and $^{125}\text{I}$ standard (with the same volume as sample) were transferred to a counting tube (5 ml) for counting $^{125}\text{I}$.

$^{129}\text{I}$ standard solution (NIST-SRM-4949c) was purchased from the National Institute Standard and Technology (Gaithersburg, MD), $^{127}\text{I}$ carrier solution with ultra-low $^{129}\text{I}$ level ($^{129}\text{I}/^{127}\text{I}$ atomic ratio $<2\times10^{-14}$) was prepared by dissolution of iodine crystal (Woodward iodine, Woodward Iodine Corporation, Oklahoma, U.S.A.) into 0.40 mol/L NaOH-0.05 mol/L NaHSO$_3$ solution. All chemical reagents used were of analytical grade, and all solutions were prepared using deionized water (18.2 MΩ·cm).

$^{125}\text{I}$ (in NaI form, no reductant) was purchased from PerkinElmer Inc. (USA). $^{125}\text{IO}_3^-$ and $^{125}\text{I}$ labeled humic acid were prepared using $^{125}\text{I}$ solution.

For preparation of $^{125}\text{IO}_3^-$ solution, 200 kBq of $^{125}\text{I}$ (NaI) solution was taken to a beaker, 0.2 ml of 10% NaClO solution was added to oxidize $^{125}\text{I}^-$ to $^{125}\text{IO}_3^-$, the solution was heated to dryness on a hotplate at 120°C to remove most of NaClO. 1.0 ml of water was added to dissolve the residue, and the solution was loaded to an anion exchange column (AG1-$\times$4, Cl$^-$ form, 2ml, Bio-Rad Laboratory, CA, USA), 2 ml of H$_2$O was added to rinse the column. $^{125}\text{I}^-$ was removed by adsorption on the column, $^{125}\text{IO}_3^-$ in the effluent and wash was collected and used as $^{125}\text{IO}_3^-$ tracer solution.

For preparation of $^{125}$I labeled humic substances, 200 humic acid (Alfa Aesar, Thermo fisher GmbH, Germany) was first dissolved in 0.01 mol/l NaOH solution. 1.0 ml of humic acid solution and 500 kBq of $^{125}\text{I}$ (0.1 ml) was added to an Iodo-Gen tube (Pierce 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
second heating zone was directly heated to 800 °C within 30 min. The ramp procedure of the first heating zone was programmed. The mid-zone heating was turn on when the temperature of the sample zone was increased to be higher than 400 °C to ensure a precise controlled temperature in the sample zone.

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

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

Iodine trapped in the NaOH solution was further separated to prepare it as AgI precipitate for AMS measurement of $^{129}$I. 1.0 mg of $^{127}$I carrier (with a $^{129}$I/$^{127}$I ratio of $< 2 \times 10^{-14}$) and 0.5 ml of 1.0 mol/l NaHSO$_3$ solution were added to the trap solution, 3.0 mol/l HNO$_3$ solution was then added to adjust pH1-2 to reduce iodate to iodide. 0.5 ml of 1.0 mol/l AgNO$_3$ solution was added to the sample solution, the formed AgI precipitate was separated by centrifuge at 3000 rpm for 5 min. 5 ml of 3 mol/l HNO$_3$ was added to dissolve the formed Ag$_2$SO$_3$ and Ag$_2$SO$_4$, and the AgI precipitate remained in the centrifuge tube was separated by centrifuge. The precipitate was further washed with 10 ml water to remove the remaining acid. After centrifuge, the AgI precipitate was transferred to a 1.5 ml centrifuge tube using water, and then separated by centrifuge. The precipitate (AgI) in the 1.5 ml centrifuge tube was finally dried at 60-70 °C (2-3 hours).

Two $^{129}$I standards with $^{129}$I/$^{127}$I atomic ratios of $(1.01 \pm 0.03) \times 10^{-11}$ and $(1.07 \pm 0.03) \times 10^{-10}$ for AMS measurement of $^{129}$I were prepared using a diluted $^{129}$I standard solution.
(NIST-SRM-4949c ) and $^{127}$I carrier (with $^{129}/^{127}$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.). $^{129}/^{127}$I atomic ratios in the prepared targets were measured by AMS using 3MV Tandem AMS system (HVEE) in the Xi’an AMS center. $^{5+}$ ions was chosen for the measurement, where $^{127}$I$^{5+}$ was measured as charges (current) using a Faraday cup and $^{129}$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]. $^{129}/^{127}$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 $^{129}/^{127}$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).
NH\textsubscript{3} solution was used as rinsing solution between samples. The detection limit of 0.01 ng/ml for \textsuperscript{127}I was obtained (calculated as 3 times of blank). Iodine concentration in the sample was calculated by correction for chemical yield in pyrolysis separation.

3. Results and discussion

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

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

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

The organic contents in the soil and sediment vary form 1\% to more than 50\% by weight. It have been reported that an explosion might happened when the temperature was quickly increased to 280-350 °C in combustion of vegetation samples [24], a similar phenomenon was also reported in the combustion of high organic soil and sediment samples [20]. This was attributed to the sudden ignition of organic substance in the tube furnace and production of large amount of combustion gas (CO\textsubscript{2}, CO\textsubscript{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 quartz furnace tube. To avoid such an accident, a slow ignition was applied by increasing the temperature in a slow rate (< 2°C/min) between 250-400 °C. Meanwhile, a mixed gas of O₂/N₂ (1:2) was flowed during the stage of ignition to reduce the ignition speed. Compressed air was not applied to reduce the ¹²⁹I blank contributed from the ¹²⁹I in the air, especially for the analysis of low-level ¹²⁹I 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 (¹²⁵I 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°C/min and remained for 30 minutes to carbonize all organic substance in the sample (Fig. 3).

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

In the RADDEC Pyrolyser system, there are three heating zones, the sample in quartz boat was put in the first zone with an independent furnace. The temperatures for carbonization and combustion discussed above are related to the temperature in the first zone. The temperature in the second zone (outlet direction) was increased to 800°C within 30 minutes after starting the experiment, i.e. before the temperature was increased over 100 °C. Any organic species of iodine or sample particles escaped from the sample boat at the first zone was decomposed to convert all iodine to gas inorganic form (I₂/HI/HIO, etc.) in the second zone of the furnace, which was trapped in the trap solution in the bubbler. Between the sample zone and second zone, there is a mid-zone, which acts as buffer to avoid the heating of the sample zone by the furnace in the second zone, and precisely control the temperature. However, when the temperature in both sample zone and second zone are increased to more than 800 °C, the second zone might be at a lower temperature compared to both sample and second zone. Therefore, the furnace in the mid-zone was turn on when the temperature of the sample zone increased to more than 400°C (after carbonization of organic substances in the sample) to ensure no condense and deposition of iodine in the working tube.

Based on these results, an optimal protocol for temperature control in the sample zone of the combustion system is presented in Fig. 3. This protocol was programmed for the first furnace in the sample zone in this system. The temperature in the third zone is set 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 O\textsubscript{2} from the mixture of N\textsubscript{2} and O\textsubscript{2} when the temperature of the sample zone reach to 400 °C.

There is a ventilation setup in RADDECE 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 RADDECE pyrolyser-4 system (with 4 parallel tubes).

3.3 Effect of flow rate of the N\textsubscript{2}/O\textsubscript{2} gases on the recovery of iodine during combustion

The flow gases of N\textsubscript{2}/O\textsubscript{2} 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 N\textsubscript{2}/O\textsubscript{2} is another key parameter affecting the recovery of iodine. The flow rate of both gases (N\textsubscript{2} and O\textsubscript{2}) can be adjusted in the RADDECE pyrolyser system. Using the optimal protocol of combustion (Fig. 3), the effect of the flow rate (for both mixed gases of N\textsubscript{2} and O\textsubscript{2} before 400 °C and O\textsubscript{2} 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 \cite{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°C. 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/ml 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 micro-
pores 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 $^{125}\text{I}$ (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, $^{125}\text{I}$ 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 $^{125}\text{Iodide}$ tracer. A similar recovery of iodine was observed when $^{125}\text{I}$ labeled humic acid was spiked as tracer compared to $^{125}\text{Iodide}$ \[20\]. In this work, we investigated the behavior of iodide, iodate and organic associated iodine during the combustion by spiking iodide-125, iodate-125 and $^{125}\text{I}$ labeled humic acid as yield tracers. The results (Table 1) show that the recovery of $^{125}\text{I}$ are equally higher than 95% for three species of $^{125}\text{I}$ 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 °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 °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
added to the sample, which also reduce the possible contamination of $^{129}$I in the analysis of low-level $^{129}$I samples.

### 3.5 Collection of iodine released from the sample during combustion

In the combustion of sample, iodine was released as gaseous iodine, which has to be collected and converted to suitable forms for measurement of iodine isotopes. Active charcoal and alkali solution have been used for collected the released iodine [15, 21]. To improve the trapping efficiency of iodine, sulfite reductant (e.g. NaHSO$_3$) has been added to the trap solution. Our results has showed a high recovery of iodine even using only water without reductant (>65%). It is well known that molecular iodine (I$_2$) has low solubility in water, and the solubility increased when iodide presents in the water to form relative stable I$_3^-$ species. Although a disproportionation reaction of I$_2$ in water can happen for forming iodide and IO$_3^-$, but it is not favorite in neutron and acidic medium. The relative high recovery of iodine in water during combustion (65%) might indicate that the released iodine is not only in form of I$_2$, but also other species such as iodate (as discussed above), iodide (e.g. HI) and HIO, which are high water solubility.

It was also observed that the recovery of iodine was improved in alkali solution, the recovery of iodine is higher than 93% when more than 0.1 mol/l NaOH was applied as trap solution. This is attributed to the disproportionation reaction of I$_2$ in the alkaline solution to form iodide and iodate. Further increasing the NaOH concentration to 0.4 mol/l NaOH can slightly improve the recovery to more than 95%. Reductant such as Na$_2$SO$_3$ or NaHSO$_3$ has been added to the trap solution to improve the trapping efficiency of iodine during the combustion [15]. This is based on the reduction of I$_2$ by sulfite to more stable iodide, therefore improving the trapping efficiency. However, our results do not show any significant improvement of recovery of iodine by addition of NaHSO$_3$ solution in the combustion of soil and sediment sample. This might because that the dominant process of iodine in the trap solution is dissolution of soluble iodide,
iodate and HIO and disproportionation of I$_2$ in alkaline solution. It has been observed that sulfite can significantly improve the trapping efficiency of iodine in the combustion of vegetation samples [24]. This was attributed to the elimination of oxidizing regents produced during combustion of vegetation, and sulfite can react with these oxidizing regents, consequently prevent the loss of iodine from the trap solution during combustion.

In some sediment samples, organic substance might be high, a trap solution of 0.40 mol/l NaOH– 0.05 mol/l Na$_2$SO$_3$ was recommended as trap solution. However, a low concentration NaOH (0.05 mol/l and Na$_2$SO$_3$ (<0.01 mol/l) should be used when low iodine and organic substance samples (e.g rock) is analyzed, because the high concentration of NaOH and Na$_2$SO$_3$ influence the measurement of $^{127}$I using ICP-MS due to matrix effect and high dilution needed.

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

In the AMS measurement of $^{129}$I, the separated iodine needs to be prepared to solid form, mixed with conductive material and pressed into a target holder for ionizing to I$^-$ ion by bombardment using Cs$^+$ in the ion source chamber. Iodine in the trap solution is often separated by solvent extraction using CCl$_4$ or CHCl$_3$, and then back-extracted to aqueous phase as iodide, which is finally precipitated as AgI precipitate for AMS measurement. CCl$_4$ and CHCl$_3$ are toxic organic solvent, a large volume of such toxic waste will be produced when a large number of samples are analyzed. Iodine collected in the trap solution present as inorganic iodine (iodide and iodate), a direct AgI precipitation was applied to separate $^{129}$I in the trap solution after reducing all iodine to iodide using Na$_2$SO$_3$ at pH 1-2. Since iodine concentrations in the terrestrial samples (soil, lake sediment and rock) are normally low (< 10 µg/g), the amount of iodine in the trap solution is too small (< 1-100 µg) to be separated by AgI precipitation due to the 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 ($^{129}$I/$^{127}$I ratio < 2×10$^{-14}$) 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$_2$SO$_3$ 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% NH$_3$H$_2$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 powder 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...
will be splashed to the ion source chamber when bombarding with Cs+ source, consequently contaminated the ion source, cause a serious cross contamination during AMS measurement [30]. Therefore, target holder made of copper is always applied for AMS measurement of $^{129}$I, because chlorine is always present in environmental samples in a large concentration compared to iodine, and some amount of AgCl is often presented in the prepared AgI target.

3.7 Detection of low-level $^{129}$I in environmental samples

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

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

Two certified reference materials, soil (IAEA-375) and sediment (NIST-4354) were analyzed using the proposed method, the results (Table 1) show that the measured $^{129}$I concentration of $(12.6 \pm 0.7) \times 10^{8}$ atom/g in soil certified reference material (IAEA-375) agrees well with the reference values of $12 \times 10^{8}$ atom/g. No $^{129}$I value was certified in the sediment NIST-4353, the measured $^{129}$I concentration of $(324 \pm 12) \times 10^{8}$ atom/g agrees well with the reported $^{129}$I concentration of $(312 \pm 43) \times 10^{8}$ atom/g in the literature [25]. This
confirms the proposed method is reliable and accurate for the determination of $^{129}$I in environmental solid samples.

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

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

The analytical results (Table 2) show a large variation of $^{129}$I and $^{127}$I concentrations and $^{129}$I/$^{127}$I ratios in these surface soil samples. The concentrations of $^{127}$I range from 0.43 to 13.47 ug/g, this might be attributed to the different types of soil. The low iodine concentration was observed in the sandy soil which was collected in the Gobi area in the Northwest China, which contains a high sand and less organic substance (ignition loss of less than 2%). The measured $^{129}$I concentrations range from $5.9 \times 10^6$ to $257 \times 10^6$ atoms/g, the high variation of $^{129}$I in the surface soil should be attributed to the different sample type and different sources of $^{129}$I. The measured $^{129}$I/$^{127}$I atomic ratios are (0.53-10.4)$\times10^{-9}$, which is comparable to the ratios in surface soil observed in Xi’an region (0.1-4.4)$\times10^{-9}$ [32] and background region of Japan (no direct contamination by nuclear facilities) in Japan. However, the measured $^{129}$I/$^{127}$I ratios are significantly higher than those measured in the surface soil collected in Chili ($10^{-12}$-$10^{-10}$) [33], this agrees with the low fallout level of radioactivity in the south hemisphere, because most of nuclear weapons tests were carried out in the North Hemisphere. In addition, the $^{129}$I released from the reprocessing plants at Sellafield (UK), La Hague (France) and others locations was also mainly deposited in the North Hemisphere, causing a high $^{129}$I level in the
North Hemisphere compared to the South Hemisphere [28, 29]. High $^{129}\text{I}/^{127}\text{I}$ ratios up to $10^{-8}$-$10^{-6}$ have been observed in the soil collected from Denmark [16], Germany [21, 33] and Slovenia [31] in the Europe, this is mainly attributed to the highly releases of two European reprocessing plants. The highest $^{129}\text{I}/^{127}\text{I}$ ratios of $10^{-7}$-$10^{-5}$ in the nuclear accident contaminated soils such as in the Chernobyl and Fukushima accident highly contaminated soil samples [11-13, 31, 34]. This indicates that the $^{129}\text{I}$ level in these soil samples from the Northwest China fall into the background level of $^{129}\text{I}$ in the North Hemisphere, it mainly originated from the global fallout of nuclear weapons tests and large-distance dispersion of reprocessing released $^{129}\text{I}$.

Acknowledgement

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References


7. Raisbeck GM. Yiou F, Zhou ZQ (1995) $^{129}$I from nuclear fuel reprocessing facilities at Sellafield (U.K.) and La Hague (France); potential as an oceanographie tracer. J Mar Sys 6(5-6): 561-570


Caption of figures:

Fig. 1 a) Schematic diagram of the Pyrolyser-4 Trio™ 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
Table 1 Separation of iodine in environmental solid samples by combustion

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

<table>
<thead>
<tr>
<th>Sample</th>
<th>Weight (g)</th>
<th>Spiked ¹²⁵I tracer</th>
<th>Recovery of ¹²⁵I (%)</th>
<th>Measured ¹²⁷I, (µg/g)</th>
<th>Certified or literature value of ¹²⁷I, (µg/g)</th>
<th>Measured ¹²⁹I (×10⁸ atom/g)</th>
<th>Certified or literature value of ¹²⁹I (×10⁸ atom/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil 5.0</td>
<td>1²⁵Iodide</td>
<td>96.4±2.6</td>
<td>2.15±0.16</td>
<td></td>
<td>1.26±0.09</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soil 20.0</td>
<td>1²⁵Iodide</td>
<td>97.8±2.1</td>
<td>2.27±0.19</td>
<td></td>
<td>1.23±0.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soil 5.0</td>
<td>1²⁵Iodate</td>
<td>95.8±3.1</td>
<td>2.09±0.08</td>
<td></td>
<td>1.24±0.10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soil 20.0</td>
<td>1²⁵Iodate</td>
<td>96.2±2.5</td>
<td>2.07±0.11</td>
<td></td>
<td>1.21±0.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soil 5.0</td>
<td>¹²⁵I-humic acid</td>
<td>96.2±2.0</td>
<td>2.11±0.11</td>
<td></td>
<td>1.28±0.09</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soil 20.0</td>
<td>¹²⁵I-humic acid</td>
<td>96.2±2.8</td>
<td>2.19±0.11</td>
<td></td>
<td>1.26±0.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sediment 5.0</td>
<td>1²⁵Iodide</td>
<td>95.4±3.5</td>
<td>15.2±0.5</td>
<td></td>
<td>7.73±0.32</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sediment 5.0</td>
<td>¹²⁵Iodate</td>
<td>95.9±2.2</td>
<td>15.9±0.6</td>
<td></td>
<td>8.00±0.28</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sediment 5.0</td>
<td>¹²⁵I-humic acid</td>
<td>96.9±2.6</td>
<td>15.4±0.7</td>
<td></td>
<td>8.12±0.31</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rock 20.0</td>
<td>1²⁵Iodide</td>
<td>97.4±3.0</td>
<td>0.560±0.022</td>
<td></td>
<td>(9.38±1.70)×10⁻³</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rock 20.0</td>
<td>¹²⁵Iodate</td>
<td>96.9±2.7</td>
<td>0.571±0.025</td>
<td></td>
<td>(10.7±1.6)×10⁻³</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soil (IAEA-375)</td>
<td>3.0</td>
<td>¹²⁵Iodide</td>
<td>97.1±2.5</td>
<td>1.83±0.08</td>
<td>1.74±0.05 (2)</td>
<td>12.6±0.7</td>
<td>12 (1)</td>
</tr>
<tr>
<td>(NIST-4354)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.85±0.77 (3)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(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.

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Sampling location</th>
<th>Latitude $^\circ$ N</th>
<th>Longitude $^\circ$ E</th>
<th>$^{127}$I conc. μg/g</th>
<th>$^{129}$I conc. $\times 10^6$ atoms/g</th>
<th>$^{129}$I/$^{127}$I atoms ratio, $\times 10^{-9}$</th>
<th>Recovery of iodine in combustion</th>
<th>Total recovery of iodine</th>
</tr>
</thead>
<tbody>
<tr>
<td>S01</td>
<td>Qingshuihe</td>
<td>37.36</td>
<td>105.62</td>
<td>0.43 ± 0.01</td>
<td>7.66 ± 0.15</td>
<td>3.78 ± 0.17</td>
<td>97.64%</td>
<td>95.86%</td>
</tr>
<tr>
<td>S02</td>
<td>Jiuduntown</td>
<td>38.18</td>
<td>102.76</td>
<td>1.07 ± 0.01</td>
<td>52.6 ± 0.4</td>
<td>10.4 ± 0.58</td>
<td>96.69%</td>
<td>86.23%</td>
</tr>
<tr>
<td>S03</td>
<td>Gangcha</td>
<td>37.27</td>
<td>100.31</td>
<td>13.5 ± 0.2</td>
<td>63.9 ± 0.5</td>
<td>1.00 ± 0.02</td>
<td>97.08%</td>
<td>94.26%</td>
</tr>
<tr>
<td>S04</td>
<td>Xiningdong</td>
<td>36.48</td>
<td>102.20</td>
<td>8.21 ± 0.06</td>
<td>41.6 ± 0.7</td>
<td>1.07 ± 0.02</td>
<td>97.86%</td>
<td>96.74%</td>
</tr>
<tr>
<td>S05</td>
<td>Jiejiazui</td>
<td>35.90</td>
<td>104.17</td>
<td>2.41 ± 0.03</td>
<td>48.1 ± 0.8</td>
<td>4.21 ± 0.10</td>
<td>97.24%</td>
<td>90.98%</td>
</tr>
<tr>
<td>S06</td>
<td>Hami</td>
<td>42.98</td>
<td>93.43</td>
<td>9.78 ± 0.36</td>
<td>257 ± 3</td>
<td>5.54 ± 0.21</td>
<td>99.50%</td>
<td>90.41%</td>
</tr>
<tr>
<td>S07</td>
<td>Weilinan</td>
<td>41.26</td>
<td>86.30</td>
<td>2.34 ± 0.04</td>
<td>5.89 ± 0.17</td>
<td>0.53 ± 0.03</td>
<td>97.96%</td>
<td>89.47%</td>
</tr>
<tr>
<td>S08</td>
<td>Yangtakelangan</td>
<td>39.79</td>
<td>88.38</td>
<td>1.30 ± 0.02</td>
<td>7.69 ± 0.16</td>
<td>1.25 ± 0.07</td>
<td>99.71%</td>
<td>90.92%</td>
</tr>
</tbody>
</table>
Fig. 1 a) Schematic diagram of the Pyrolyser-4 Trio™ 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.
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