

Measurement of ^{129}I Radioactivity in Groundwater of Radioactive Waste Disposal Site

Mun Ja KANG*, Kun Ho CHUNG, Wannoo LEE, Doo Won PARK, Hee Reyoung KIM, Chang Woo LEE, and Geun Sik CHOI

*Korea Atomic Energy Research Institute,
1045 Daedeok-daero, Yuseong-gu, Daejeon, 305-353 Korea*

The investigation of the environmental radioactivity around the radioactive waste disposal site in Gyeongju is being carried out. The radioactivity of ^{129}I in groundwater and seaweed are to be measured. The analytical method to measure the radioactivity of ^{129}I in aqueous media was established. This method contains oxidation-reduction reaction, anion-exchange separation and palladium precipitation. The ^{129}I radioactivity in the PdI_2 precipitates was measured by using low-energy gamma spectrometer. The counts of peak at 39.6 keV of gamma energy were used for determination of ^{129}I radioactivity. The chemical recovery was determined by the weights of PdI_2 precipitates. The deionized water and groundwater spiked with ^{129}I tracer were tested. In the case of deionized water, the relative deviations of measured concentration from spiked one are from 1.1 to 10.7%. The relative deviations of measured radioactivity from spiked one in the groundwater experiments are 2.9 and 3.7%. The measured concentration is in good agreement with spiked one. The groundwater sampled from radioactive waste disposal site was tested. The concentrations of ^{129}I in the groundwater are below minimum detectable activities of 36.7 and 36.6 mBq/L.

KEYWORDS: *iodine-129, low-energy gamma spectrometer, PdI_2 precipitate, environmental radioactivity*

I. Introduction

The investigation of the environmental radioactivity around the radioactive waste disposal site in Gyeongju is being carried out. The purpose of this investigation is to obtain base-line data of radioactivity in the step of pre-operation of the disposal facility. The environmental radioactivity including gross α , gross β , ^3H , ^{14}C , ^{90}Sr , γ -ray emitting radionuclides, U, and $^{239+240}\text{Pu}$ are analyzed routinely in various environmental samples. In addition, ^{99}Tc and ^{129}I are to be measured for groundwater and seaweed.¹⁾

The nuclide ^{129}I is produced mainly by spontaneous fission of uranium and by cosmic ray interaction with xenon in the atmosphere. In addition to these, considerable amounts of artificial ^{129}I have also been discharged into the environment due to nuclear weapon test and partially by the operation of nuclear facilities. Since the half-life of ^{129}I is very long (1.6×10^7 years), it is expected that this nuclide would accumulate in the environment. When the radioiodine is ingested into the human body, it is concentrated in the thyroid gland. It is important to obtain information on accumulation of this nuclide in the environment.²⁾

The only stable isotope of iodine is ^{127}I and the most long-lived radioisotope of iodine is ^{129}I . Human nuclear activity has produced and released a large amount of ^{129}I to the environment thus elevating the $^{129}\text{I}/^{127}\text{I}$ ratio by at least 2 orders of magnitude compared with the natural values.³⁾ Due to the long half-life and high mobility in stored radioactive waste, ^{129}I is important radionuclide in the waste

management. The amount of ^{129}I in surface water has increased due to release from nuclear fuel reprocessing facilities. Discharges from nuclear reprocessing facilities are responsible for about 90% of the ^{129}I environmental inventory.⁴⁾

Atmospheric ^{129}I emissions from nuclear facilities also occur and are difficult to monitor. However, moss and lichen, which derive their nourishment entirely from the atmosphere, should be in equilibrium with airborne iodine, and therefore offer a means to measuring ^{129}I emissions.⁵⁾ In addition, the behavior of iodine in the secondary environment must be considered. The secondary environment is derived from the oceans by way of the atmosphere, and as result near-coastal soils and surface water. It appears that appreciable quantities of iodine recycled from soils, lakes and river by volatilization.

Many researchers have studied the determination of ^{129}I and ^{127}I ratio in various environmental samples to evaluate the effect of nuclear activities.^{2, 4, 5, 6)} For the measurement of ^{129}I radioactivity, the radiochemical neutron activation analysis (NAA) and accelerator mass spectrometry (AMS) have been used. In the case of neutron activation analysis, iodine was extracted from environmental samples, and irradiated in a thermal neutron flux density of $5 \times 10^{13} \text{ n cm}^{-2} \text{ s}^{-1}$. The concentrations of ^{129}I and ^{127}I were determined from those of ^{130}I and ^{126}I .^{2, 6, 7)} AMS was also used to measure the ^{129}I and ^{127}I radioactivity after pretreatment.^{4, 5)}

Measurement of ^{129}I can be carried out by an X-ray detector and liquid scintillation counter. The most common technique is a low-energy gamma spectrometry. Gamma spectrometry has been used to measure ^{129}I in thyroid, urine, seaweed, and wastes.⁸⁾ Due to the low counting efficiency

* Corresponding author, Tel.: +82-42-868-2078 Fax.: +82-42-863-1289 E-Mail: munkang@kaeri.re.kr

of the detector, low γ -ray yield and high background, a high detection limit was obtained. A chemical separation of iodine from the matrix and interfering radionuclides can improve the detection limit to around 20 mBq. For the gamma counting, the iodide anion in the sample has been converted to PdI_2 precipitate or AgI precipitate. The iodine was separated by CCl_4 extraction or anion exchange.^{2, 3, 4, 7, 9)} These methods have been used for the separation of ^{129}I in the analysis using NAA or AMS. In this study, the oxidant and reductant were used for the fixation of iodine species in the water. Iodide anion was precipitated as PdI_2 for gamma counting. An anion exchange method was adapted for the separation of iodide.

II. Experiments

1. Chemical separation of iodine

The aqueous sample was evaporated to the volume below 250 ml. Carrier solutions of iron, cobalt and iodide were added to the aqueous sample. Iodide carrier of 30 mg was used. Iodide carrier solution was prepared by solving NaI to deionized water. A series of hydroxide precipitation reactions was then carried out using ammonia solution to precipitate iron hydroxide and sodium hydroxide to precipitate cobalt hydroxide. In each precipitation stage, the hydroxide precipitate was removed by centrifugation. NaOCl solution was then added to the resulting solution to ensure that iodine in solution is present in the form of periodate. The periodate solution was then reduced to iodide by the sequential addition of $\text{H}_2\text{NOH}\cdot\text{HCl}$ solution and $\text{Na}_2\text{S}_2\text{O}_5$ solution. The resulting solution was adjusted to a pH value of 6.5. When the pH-adjusted solution was passed through an anion-exchange column, the sorption of iodide anion occurs. The column was then sequentially washed with deionized water and NaCl solution. Iodine-129

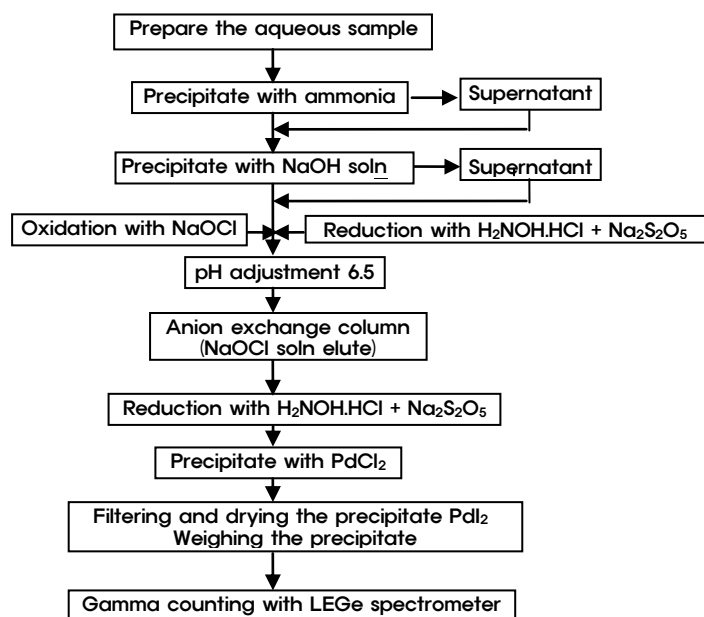


Fig. 1 Schematic diagram for the determination of ^{129}I using oxidation-reduction, chromatography and precipitation method

was eluted with NaOCl solution. The elute was collected in a beaker and the iodine was precipitated as PdI_2 using PdCl_2 solution. The PdI_2 precipitate was filtered, dried and mounted on an aluminum planchette before it is counted on a low-energy gamma detector (LEGe spectrometer). The schematic diagram for the determination of ^{129}I in aqueous media is shown in Fig. 1.

2. Determination of ^{129}I radioactivity

The ^{129}I radioactivity of PdI_2 precipitate was measured by using LEGe spectrometer (ORTEC GMX30P4). The gamma and X-ray energies of ^{129}I are 27.8, 29.5, 33.6, 34.6, and 39.6 keV. The counts at the energy of 39.6 keV are used for the radioactivity determination. The spectrum of ^{129}I at the range of gamma and X-ray energy are shown in Fig. 2. The peaks in square are the ones of ^{129}I . The right dark peak is corresponding to the energy of 39.6 keV. This peak is identical to that of ^{129}I .

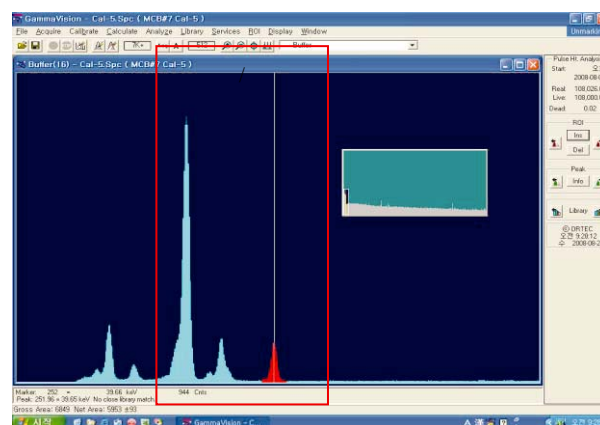


Fig. 2 The spectrum of gamma and X-ray energy of ^{129}I

3. Measurement of ^{129}I in the groundwater

For the validation of the analytical procedure, the measurement of ^{129}I radioactivity in the spiked distilled water and spiked groundwater was carried out. Sample volume was varied from 50 ml to 10 L. The known radioactivity using ^{129}I tracer was added to the samples. The chemical separation was carried out by the above procedure. The PdI_2 precipitate containing ^{129}I was obtained. The ^{129}I radioactivity was measured by LEGe spectrometer. The weight of PdI_2 was measured for the determination of recovery. The measurement of ^{129}I in the groundwater sampled from radioactive waste disposal site of Gyeongju was then performed. The groundwater of 10 L was used.

III. Results and Discussion

1. Efficiency of LEGe spectrometer

For the determination of the efficiency of LEGe spectrometer, the PdI_2 precipitates with different PdI_2 weight were prepared. The PdI_2 precipitates include known radioactivity of ^{129}I tracer. The efficiency of LEGe spectrometer as a function of weights of PdI_2 precipitate was calculated. The efficiency is varied from 0.8 to 1.5% because of self-absorption of PdI_2 precipitate. The linear

relationship between the efficiency and weight of PdI₂ precipitate was obtained. The relationship is shown in Fig. 3. The calculated equation is $y = -0.0000121x + 0.015780$ ($r^2 = 0.9886$).

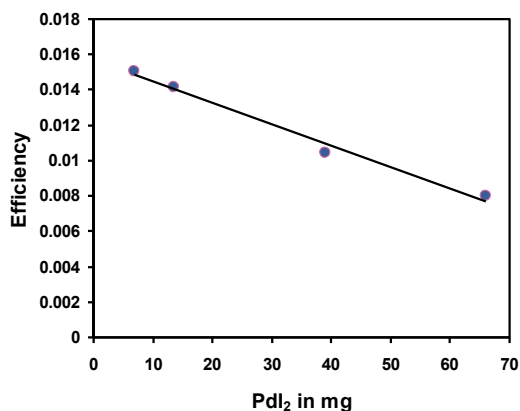


Fig. 3 The efficiency of LEGe spectrometer as a function of weight of PdI₂ precipitate

2. Calculation of ¹²⁹I radioactivity

The radioactivity of ¹²⁹I in the groundwater samples, A (Bq/L), was calculated by the following equation.

$$A = \frac{\left(\frac{G}{t_s} - \frac{B}{t_b}\right)}{\frac{CE}{100} \times \frac{Y}{100} \times V}$$

The minimum detectable activity (MDA) value is determined by following Currie's equation.¹⁰⁾

$$MDA = \frac{4.65 \sqrt{\frac{B}{t_b} \times t_s}}{t_s \times \frac{CE}{100} \times \frac{Y}{100} \times V}$$

G and B are gross counts of sample in planchette and background counts of planchette, respectively. t_s and t_b are count time of gross counts of sample and background counts, respectively. CE means the percent efficiency of LEGe spectrometer. Y is the recovery of the chemical separation using the weight of PdI₂ precipitate. V is the volume of groundwater.

3. Measurement of ¹²⁹I radioactivity in the spiked water

Radioactivity of ¹²⁹I was measured in the deionized water spiked with known ¹²⁹I tracer. The concentration of spiked ¹²⁹I and measured ¹²⁹I and the relative deviation between these concentrations are summarized in Table 1. The chemical recoveries are also listed. 50 ml deionized water spiked with ¹²⁹I tracer was tested. The spiked concentration is varied from 4.5 Bq/L to 133 Bq/L. From the experimental results, the chemical recoveries are obtained above 83.8 %. The relative deviation of measured

concentration and spiked one is from 1.1 to 10.7%.

Table 1. Experimental results of ¹²⁹I radioactivity measurement in the spiked water

Samples	Sample Volume (ml)	Chem. Yield (%)	Spiked Radio-activity (Bq/L)	Measured Radio-activity (Bq/L)	Rel. Devia-tion (%)
Blank	50	87.9	-	-	-
Spiked 1	50	83.8	6.75	6.03±0.480	10.7
Spiked 2	50	87.7	27.2	26.9±2.23	1.1
Spiked 3	50	85.7	133	130±7.87	2.8
Spiked 4	150	92.5	4.50	4.73±0.348	5.1

4. Measurement of ¹²⁹I radioactivity in the spiked groundwater

Radioactivity of ¹²⁹I was measured in the groundwater spiked with known ¹²⁹I tracer. The experimental results of ¹²⁹I radioactivity measurement in the spiked samples are summarized in Table 2.

Table 2. Experimental results of ¹²⁹I radioactivity measurement in the spiked groundwater

Samples	Sample Volume (ml)	Chem. Yield (%)	Spiked Radio-activity (mBq/L)	Measured Radio-activity (mBq/L)	Rel. Devia-tion (%)
Blank	150	96.0	-	-	-
Spiked 1	10,000	41.9	67.8	65.8±4.97	2.9
Spiked 2	10,000	55.1	67.9	65.4±5.05	3.7

The groundwater spiked with ¹²⁹I tracer was used for the validation of this analytical procedure. Groundwater of 10 L was evaporated to the volume of below 250 ml. The spiked radioactivities of ¹²⁹I are 67.8 and 67.9 mBq/L and the measured radioactivities are 65.8 and 65.4 mBq/L, respectively. The relative deviation of spiked and measured concentration is 2.9 and 3.7 %. The measured radioactivity is good agreement with spiked one. In this experiment, the chemical recoveries are 41.9 and 55.1 %. This recovery is lower than the recovery from experiments of the deionized water. Low chemical recovery may be caused by the chemical species of iodine in the water. In the water, the iodine exists as iodide anion, iodate anion and organic iodine compound. Iodide is a thermodynamically unstable species in oxygenated water. The mechanism of conversion among iodine species is still not clear because of the difficulties associated with distinguishing the origin of newly produced and converted iodine species.^{3, 4, 7)} It is possible that the chloride anion competes with iodide anion in the separation step.

5. Measurement of ¹²⁹I radioactivity in the ground-water

Radioactivity of ^{129}I was measured in the groundwater sampled in the radioactive waste disposal site, Gyeongju. The experimental results of ^{129}I radioactivity measurement in the groundwater samples are summarized in **Table 3**.

Table 3. Experimental results of ^{129}I radioactivity measurement in the groundwater sampled from the disposal site

Samples	Sample Volume (ml)	Chem. Yield (%)	Measured Radioactivity (mBq/L)
DB1-1	10,000	15.3	20.9±2.61
PW2	10,000	16.0	11.3±2.06

The groundwater sampled in the disposal site was analyzed. These samples were collected from the boring core at the depth of 205 and 120 m. There are 6 boring cores for sampling groundwater to test radionuclide monitoring. Groundwater of 10 L was collected and evaporated to the volume of below 250 ml. The chemical separation and counting the radioactivity were carried out by the described procedure above. The radioactivity of ^{129}I in the groundwater is measured as 20.9 and 11.3 mBq/L. These values are below MDA. The MDA values are 36.6 and 36.7 mBq/L. This is calculated as above equation by Currie. And the counting time for LEGe spectrometer was 200,000 seconds. In this experiment, the chemical recoveries are 15.3 and 16.0 %. These recoveries are a little low comparing the experimental results of the deionized water and spiked groundwater. Low chemical recovery may be caused by the chemical species of iodine in the groundwater.

IV. Conclusions

The analytical method to measure the radioactivity of ^{129}I in aqueous media was established. This method includes oxidation-reduction reactions of iodine, chromatographic separation using anion-exchange resin, and palladium precipitation. The ^{129}I radioactivity in the PdI_2 precipitate was measured by using LEGe spectrometer. The counts of peak at 39.6 keV of gamma energy were used for determination of ^{129}I radioactivity. The chemical recovery of this method was determined by the weights of PdI_2 precipitates. The efficiency of LEGe spectrometer was calculated by measuring the ^{129}I radioactivity of different weights of PdI_2 precipitates. The deionized water and groundwater spiked with ^{129}I tracer were tested for the validation of the analytical procedure. In the case of deionized water, the relative deviations of spiked

concentration and measured one are from 1.1 to 10.7 %. The relative deviations of spiked radioactivity and measured one in the experiments of spiked groundwater are 2.9 and 3.7 %. The measured concentration is in good agreement with the spiked one. The groundwater sampled in radioactive waste disposal site, Gyeongju was tested. The radioactivity of ^{129}I in the groundwater is below MDA. The MDA values are 36.7 and 36.6 mBq/L. Groundwater of 10 L was used. And the counting time for LEGe spectrometer was 200,000 seconds. Different groundwater samples from disposal sites will be adapted to this analytical method. The chemical recovery of the groundwater is to improve.

Acknowledgements

This work has been carried out under the Nuclear R&D program by MOST.

References

- 1) J. S. Baek, Y. Y. Jeong, S. B. Ahn, and W. Kim, "Radiological environment investigation of radioactive waste disposal facility," *J. of the Korean Radioactive Waste Society*, 6(4), 387 (2008), [in Korean].
- 2) Y. Muramatsu, Y. Ohmomo, and M. Sumiya, "Determination of iodine-129 and iodine-127 in environmental samples collected in Japan," *Journal of Radioanalytical and Nuclear Chemistry*, 123, 1, 181 (1988).
- 3) X. Hou, V. Hansen, A. Aldahan, G. Possnert, O. C. Lind, and G. Lujanienė, "A review on speciation of iodine-129 in the environmental and biological samples," *Analytica Chimica Acta*, 632, 181 (2009).
- 4) X. Hou, A. Aldhan, S. P. Nielsen, G. Possnert, H. Nies, and J. Hedfors, "Speciation of ^{129}I and ^{127}I in seawater and implications for sources and transport pathways in the North Sea," *Environ. Sci. Technol.* 41, 5993 (2007).
- 5) J. Rucklidge, L. Kilius, and R. Fuge, " ^{129}I in moss down-wind from the Sellafield nuclear fuel reprocessing plant," *Nuclear Instruments and Methods in Physics Research B*, 92, 417 (1994).
- 6) J. Handl, E. Oliver, D. Jakob, K. L. Johanson, and P. Schuller, "Biospheric ^{129}I concentration in the pre-nuclear and nuclear age," *Health Physics*, 65, 3, 265 (1993).
- 7) X. Hou, H. Dahlgaard, B. Rietz, U. Jacobsen, S. P. Nielsen, and A. Aarkrog, "Determination of chemical species of iodine in seawater by radiochemical neutron activation analysis combined with ion-exchange pre-separation," *Anal. Chem.*, 71, 2745 (1999).
- 8) J. A. Suárez, A. G. Espartero, M. Rodríguez, "Radiochemical analysis of ^{129}I in radioactive waste streams," *Nuclear Instruments and Methods in Physics Research A* 369, 407 (1996).
- 9) Y. Muramatsu, Y. Takada, H. Matsuzaki, and S. Yoshida, "AMS analysis of ^{129}I in Japanese soil samples collected from background areas far from nuclear facilities," *Quaternary Geochronology*, 3, 291 (2008).
- 10) L. Currie, "Limits of qualitative determination and quantitative determination," *Anal. Chem.*, 40(3), 586 (1968).