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NEUTRON ACTIVATION ANALYSIS OF IODINE-129 AND IODINE-127 IN ENVIRONMENTAL SAMPLES

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An analytical method for ^{129}I and ^{127}I in various environmental samples is described. The method consists of sample digestion by alkali fusion, iodine separation by solvent extraction, neutron irradiation, radiochemical purification of iodine and gamma-spectrometry. The detection limit of ^{129}I and the ^{129}I/^{127}I ratio are $1\cdot 10^{-3}$ pCi and $1\cdot 10^{-9}$, respectively. The range of the ^{129}I/^{127}I ratios obtained in the environmental samples collected from the Tokaimura area in Japan was between $1\cdot 10^{-9}$ and $7.9\cdot 10^{-6}$. The highest ratio was observed in pine needles followed by rain water, soil, swamp water and algae.

Introduction

Iodine-129 is produced in nature mainly by spontaneous fission of uranium and by cosmic ray interaction with xenon in the atmosphere. Owing to its long half-life ($1.6 \cdot 10^7$ years), it is expected that ^{129}I may behave similarly to stable iodine (^{127}I) in the biogeochemical cycle. Therefore, the level of ^{129}I in the environment is often expressed as the isotope ratio of ^{129}I/^{127}I. The natural ^{129}I/^{127}I ratios[1,2] for pre-atomic age lie between 10^{-12} and 10^{-15}.

Due to nuclear weapons tests and partially the operation of nuclear facilities, such as spent fuel reprocessing plants, considerable amounts of artificial ^{129}I have been added to the environment. Several papers have been presented for ^{129}I in the USA[3-7] and in the Federal Republic of Germany,[2,8,9] where high isotope ratios, sometimes more than 10^{-6}, were found in the vicinity of nuclear reprocessing plants. Only a few data were reported in Japan.[10]

From the viewpoint of environmental surveillance and radiation safety[11-13], it is required to develop a reliable and practical method for the determination of ^{129}I and ^{127}I in environmental samples. Possible detection methods are X-ray counting,[14] liquid scintillation counting,[4,15] mass-spectrometry[16] and neutron activation analysis.[2,3,8,17] The former two are applicable only when significant quantities of ^{129}I are contained in the sample. The neutron activation analysis offers advantages[18,19] for sensitive and simultaneous determination of both ^{129}I and ^{127}I.

This element is volatile and chemically unstable, so special attention must be paid to the pretreatment of the sample. For example, BRAUER et al.[3,18] and AUMANN et al.[2] used the combustion method, that is, iodine was evaporated from the sample by heating at 1000 °C in oxygen followed by trapping on activated charcoal and subsequent chemical separation for irradiation. They measured ^{129}I and ^{127}I by coincident spectrometry technique after purification of the irradiated iodine. The detection limit was about $1 \cdot 10^{-12}$ as $^{129}I/^{127}I$ ratio. Their method is sensitive and attractive excluding water samples, but a specially designed combustion equipment and the coincident spectrometry system are required.

In order to obtain a readily applicable method for the determination of ^{129}I by using common radiochemical apparatus and reagents, the important steps in the analytical procedure such as (a) sample digestion, (b) iodine separation, (c) irradiation, (d) radiochemical purification and (e) gamma-spectrometry were examined. This paper also describes the concentration of ^{129}I and ^{127}I in several environmental samples collected from the Tokaimura area in Japan, where several kinds of nuclear facilities such as power reactors, research reactors, spent fuel reprocessing plant, etc., are located.

Experimental

Sample digestion

The plant sample such as alga or pine needle (5 to 40 g on dry basis) was mixed in a nickel crucible with deionized water, ethanol and potassium hydroxide (about twice the weight of the sample). The soil sample (1 to 6 g on dry basis) was crushed, sieved ($\leqslant$0.2 mm) and moistened with deionized water in a nickel crucible and mixed with potassium hydroxide (10 to 30 g). The water sample (40 to 60 liter) was first mixed with potassium hydroxide (about 20 g) in an large evaporation dish before reducing the volume of the sample by heating. Then the sample was transferred into a nickel crucible. For the determination of chemical yield, ^{125}I was added to each sample as a tracer.

The samples in the crucibles were dried on a hot plate, under stirring with a glass rod. Then they were heated gradually to about 650 °C in a muffle furnace and maintained at this temperature for about 30 min to burn and fuse the sample.

Iodine separation prior to the irradiation

After cooling to room temperature, about 50 ml of deionized water was added into the crucible and heated on a hot plate to dissolve the iodine, then the solution was filtered on a glass, filter (Whatman GF/F). A 1 ml of a 5% sodium sulfite solution was added to the filtrate to reduce iodine to iodide, afterwards the solution was acidified with nitric acid. To obtain better recovery, it is necessary to check the activity of the residue. If considerable activities are left, both residue and the inside of the crucible should be washed with sodium sulfite solution and nitric acid in order to dissolve iodine. The washings should be filtered and combined with the solution obtained above. During the acidification, a silica precipitate sometimes appeared in the solution. In this case, the solution should be centrifuged and filtered to remove the precipitate.

The solution was introduced into a 100 ml separatory funnel to which 30 ml of carbon tetrachloride and 1 ml of a 0.5M sodium nitrite solution were added. Iodine was extracted into the organic phase by shaking. The organic phase was drawn off into another separatory funnel. The extraction procedure was repeated 1 to 3 times with 10 to 20 ml of carbon tetrachloride and 0.5 ml of a 0.5M sodium nitrite solution to extract iodine from the aqueous solution as completely as possible. The extraction rate of iodine was checked with the activity of ^{125}I in the solution. These organic phases were combined in a separatory funnel and the iodine was back-extracted twice with 15 ml of a 0.05% sodium sulfite solution. These aqueous phases were acidified and combined in another separatory funnel. The extraction process of iodine with carbon tetrachloride was repeated. Then the iodine in the organic phase was back-extracted twice with 10 ml of a 0.02% sulfurous acid solution as iodide. A small amount of lithium hydroxide was added to the aqueous phase in order to prevent the loss of iodine. The solution in a small beaker was carefully evaporated to about 0.3 ml on a hot plate and transferred into a quartz ampoule shown in Fig. 1. The yield of pre-irradiation chemistry was determined by the measurement of ^{125}I with NaI scintillation counter. Standard samples containing known amounts of ^{129}I and ^{127}I were prepared by the addition of a small amount of lithium hydroxide, then transferred into the ampoule.

The samples and standards were freeze-dried, then the upper neck of the ampoule (a of the Fig. 1) was sealed.

Irradiation

Samples and standards were irradiated simultaneously at a thermal neutron flux of $5.5 \cdot 10^{13}$ n cm^{2} sec for 6 hrs in the JRR–4 reactor, of the Japan Atomic Energy Research Institute.

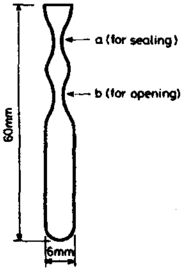

Fig. 1. Scheme of the quartz ampoule for irradiation

Radiochemical purification of iodine

After about 17 hrs cooling period, the ampoule was opened in a beaker containing 30 ml of deionized water, 1 ml of a 5% sodium hydrosulfite solution, 3 ml of KI solution (10 mg I/ml) and 1 ml of KBr solution (10 mg Br/ml). The irradiated sample was dissolved in the solution. The ampoule was further washed with 10 ml of a 0.2M potassium hydroxide solution. The solutions were combined in a separatory funnel, and then acidified with nitric acid. 20 ml of carbon tetrachloride and 1 ml of a 0.5M sodium nitrite solution were added to the solution and shaken vigorously. The iodine was extracted into the organic phase. This procedure was repeated twice with 10 ml of carbon tetrachloride and 0.5 ml of a 0.5M sodium nitrite solution. Then the iodine was back-extracted from the organic phase twice with the 20 ml of a 0.05% sodium hydrosulfite solution as iodide. These organic solvent extraction and back-extraction processes were repated again in order to remove radioactive contaminants such as activated bromine and sodium

Finally the iodine was precipitated as PdI_2 by the addition of 2 ml palladium chloride solution (20 mg Pd/1 ml of 3N HCl). It was filtered on a glass filter, then washed with deionized water and ethanol and dried at 105 °C. The chemical yield during the post-irradiation chemistry was examined gravimetrically.

The standard samples were treated by the same procedure as above.

Gamma-spectrometry

The ^{130}I and ^{126}I, which were produced from ^{129}I and ^{127}I by irradiation, were measured gamma-spectrometrically, using a Ge-detector coupled to a 4096-channel pulse-height analyzer. The counting time was 80 to 200 min.

Results and discussion

Sample digestion

The loss of iodine from the sample during the alkali fusion was about 5 to 20%. In general, the rate of iodine volatilization from algae was small, while that from terrestrial plants was large. The loss is related to the temperature of the furnace, the heating time, the sample size, the iodine concentration and probably chemical forms of iodine. The heating time and temperature should be chosen in accordance with the variety and the size of the sample. To reduce iodine losses, it can be recommended that the sample should be divided into small portions to digest the sample in a short time.

Iodine separation prior to irradiation

It is necessary to purify iodine as far as possible before irradiation in order to reduce the production of radioactive contaminants. The solvent extraction method is suitable for this purpose. The recovery in the process of the extraction and the back-extraction was more than 95% for algae sample, whereas that for soil and terrestrial plant samples was sometimes lower than 75%. The extraction rate may be dependent on the iodine concentration and the matrix of the sample.

The sample for irradiation is often sealed in a small quartz ampoule as I_2. However, it seems not so easy to trap I_2 quantitatively in a small quartz ampoule. Therefore, for convenience we adopted to fix iodine as iodide in a quartz ampoule by freeze-drying method. In order to check the loss of iodine from the ampoule by freeze-drying, various types of reagents were added to the solution containing $^{125}I^-$ as a tracer. No significant losses were observed when alkali hydroxide such as potassium or lithium hydroxide was added to the solution. Production of radioactive contaminants from lithium is obviously smaller than that from potassium. Therefore, lithium hydroxide was added to the solution prior to freeze-drying for preventing the loss of iodine.

Neutron irradiation

The important reactions occurring are as follows:

$$
\begin{aligned}
&{}^{129}\mathrm{I}\,(n,\gamma)\,{}^{130}\mathrm{I} \xrightarrow[12.3\ \mathrm{h}]{} {}^{130}\mathrm{Xe}\\
&{}^{127}\mathrm{I}\,(n,\gamma)\,{}^{128}\mathrm{I} \xrightarrow[25\ \mathrm{m}]{} {}^{128}\mathrm{Xe}\\
&{}^{127}\mathrm{I}\,(n,\gamma)\,{}^{126}\mathrm{I} \xrightarrow[13\ \mathrm{d}]{} {}^{128}\mathrm{Xe}
\end{aligned}
$$

The ^{128}I decayed out during the cooling period. The radiations of ^{130}I and ^{126}I were used for the determination of ^{129}I and ^{127}I, respectively.

The ^{130}I is possibly produced by the reaction ^{127}I(3n, γ)^{130}I. We have irradiated 5 mg of stable iodine chemicals to check the effect of the reaction under the irradiation conditions. But the production of ^{130}I was below the limit of detection. AUMANN et al.[2] also reported that the interference due to triple neutron capture can be ignored for the measurement of ^{129}I in environmental levels. ^{130}I will also be produced by the reactions ^{235}U(n, f)^{129}I(n, γ)^{130}I, ^{133}Cs(n, α)^{130}I and ^{128}Te(n, γ)^{129}Te $\xrightarrow{\gamma,\beta}$ ^{129}I(n, γ)^{130}I. However, the contaminants such as U, Cs and Te have been removed by the chemical procedures prior to the irradiation.

Some authors used ^{131}I as tracer for the determination of chemical yield. We found about 5 pCi of ^{129}I contaminants in the vial of ^{131}I(New England Nuclear NEZ–035H, original concentration: 1mCi). Therefore, the use of a large amount of ^{131}I as tracer should be avoided for the analysis of low level ^{129}I. The ^{126}I produced by the ^{125}I(n, γ)^{126}I reaction is also a possible interference, but it was actually negligible.

Radiochemical purification of iodine

Palladium ion is thought to be more suitable than silver ion to fix the iodine, because a homogeneous precipitate was obtained on the glass filter and it is also possible to avoid co-precipitation of bromine contaminants. The iodine recovery in the post-irradiation procedure was more than 95%.

Gamma-spectrometry

Fig. 2 shows examples of the spectra obtained for standard (^{129}I/^{127}I ratio: 10^{-6}), soil and algae samples. It is clear that iodine was successfully separated. The interference from radioactive bromine could be eliminated by the chemical procedure. The concentrations of ^{129}I and ^{127}I in the sample were determined from the activities of ^{130}I (418, 536 and 739 keV peaks) and ^{126}I (389, 491 and 754 keV peaks), respectively.

The detection limit of ^{129}I and the ^{129}I/^{127} ratio were $1 \cdot 10^{-3}$ pCi and $1 \cdot 10^{-9}$, respectively. But they are influenced by many factors such as sample variety, stable iodine content, irradiation time and neutron flux. The chemical yields throughout the procedure were 70 to 90% for algae samples and 50 to 80% for pine needle, soil and water samples.

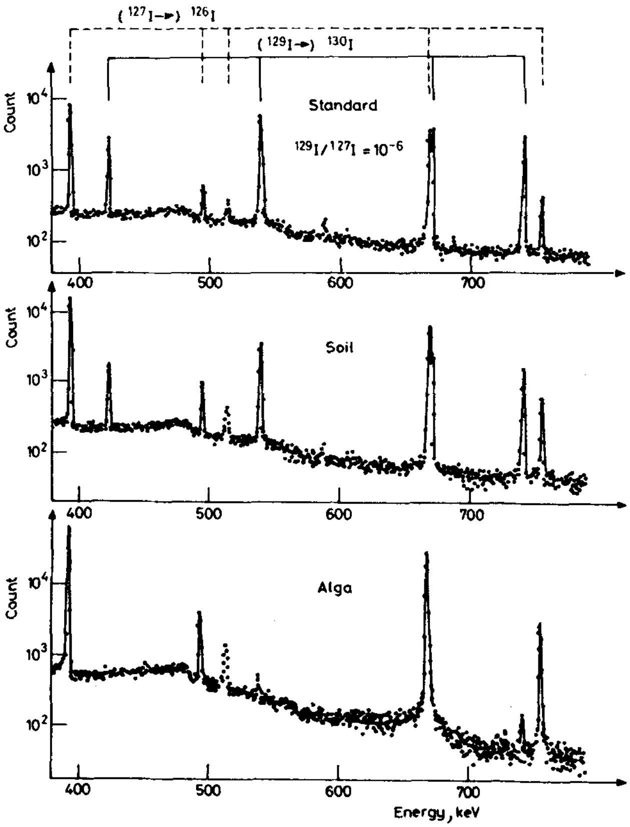

Fig. 2. Gamma-spectra of a standard, a soil and an alga sample. Standard sample containing 0.17 pCI of ^{129} and 1 mg of ^{127}I. Soil sample was collected from Tokaimura(B) and algae(Hijiki) sample from Nakaminato

Table 1 shows the analytical results for ^{129}I and ^{127}I in the environmental samples collected from the Tokaimura area / Ibaraki Prefecture. The highest ^{129}I/^{127}I ratio was observed in pine needles followed by rain water, swamp water, soil and algae. It was observed that the ^{129}I/^{127}I ratio in algae was related to the vertical distribution of the algae on the sea shore. The ^{129}I/^{127}I ratio decreased in the order Funori (*Gloiopeltis furcata*), Hijiki (*Hizikia fusiforme*) and Wakame (*Undaria pinnatifida*), collected from upper littoral belt, from lower littoral belt and from upper sublittoral belt, respectively. It is supposed that the algae of the littoral belt were influenced by the deposition of terrestrial ^{129}I.

Table 1

^{129}I and ^{127}I in environmental samples collected from the Tokaimura area

Sample / Location	Date of Sampling	^{127}I, ppm	^{129}I, 10^{-3} pCi/kg or l	$^{129}I/^{127}I$, ratio
Pine needle(fresh) / Tokaimura	Sep. 1981	0.41	560	$7.9 \cdot 10^{-6}$
Pine needle(fresh) / Nakaminato	Sep. 1981	0.34	33	$5.6 \cdot 10^{-7}$
Soil(dry) / Tokaimura(A)	Sep. 1981	20	1100	$3.1 \cdot 10^{-7}$
Soil(dry)* / Tokaimura(B)	Apr. 1981	5.7	320	$3.2 \cdot 10^{-7}$
Sandy-Soil(dry)* / Tokaimura	Apr. 1981	0.7	180	$1.5 \cdot 10^{-6}$
Funori-Algae(wet) / Nakaminato	Apr. 1982	28	25	$5.1 \cdot 10^{-9}$
Hijiki-Algae(wet) / Nakaminato	Jul. 1981	43	25	$3.3 \cdot 10^{-9}$
Wakame-Algae(wet) / Nakaminato	Apr. 1982	7.3	1	$<1 \cdot 10^{-9}$
Rain Water / Tokaimura	Sep. 1979–Mar. 1981	0.0034	3.0	$5.0 \cdot 10^{-6}$
Swamp Water / Tokaimura	Jul. 1981	0.0031	0.083	$1.6 \cdot 10^{-7}$

*After leaching of the sample (about 200 g) with a 3% KOH solution (about 500 ml) on a hot plate, the supernatant was used.

The detection by a single Ge-detector was not as sensitive as that by coincident counting systems, however, this analytical method was evidently applicable to the determination of ^{129}I in several kinds of environmental samples by using common radiochemical equipment and reagents.

The analyses of ^{129}I in the environment of Japan are now in progress and the data will be presented elsewhere.

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