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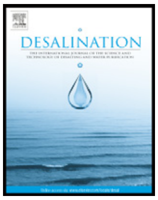

Progress on ^{129}I analysis and its application in environmental and geological researches

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ABSTRACT

Iodine-129 is a naturally generated isotope, but anthropogenic releases are the dominated source of ^{129}I in the present environment. Among many measurement techniques, neutron activation analysis (NAA) and accelerator mass spectrometry (AMS) are only methods used for measurement of ^{129}I in environmental level. Based on its source terms, chemical properties and environmental behaviors, ^{129}I can be applied for geological dating in a range of 2–80 Ma, investigation of formation and migration of hydrocarbon, circulation of ocean water, atmospheric process of iodine, as well as reconstruction of dispersion and migration of short-lived radioisotopes of iodine released from nuclear accidents. This article aims to summarize and critically compare the analytical techniques used for ^{129}I measurement and chemical methods for separation of iodine from various sample matrices, purification from the interferences, as well as preparation of suitable target for AMS measurement. The major applications in environmental and geological researches are reviewed, which mainly focus on the new progress and potential development in the future. The application of ^{129}I in the investigation of radioactive contamination from the Fukushima accident is discussed.

1. Introduction

^{129}I, a long-lived radioisotope of iodine ($t_{½} = 15.7$ Ma), is naturally generated via cosmic ray reactions with xenon in the upper atmosphere, spontaneous fission of ^{238}U, thermal neutron-induced fission of ^{235}U and to a lesser extent neutron activation reactions of tellurium, i.e. $^{128}\text{Te}(n, \gamma)^{129}\text{Te}(\beta^-)^{129}\text{I}$ and $^{130}\text{Te}(n, 2n)\ ^{129}\text{Te}(\beta^-)^{129}\text{I}$ in the earth. The total inventory of the natural ^{129}I in the earth was estimated to be ~50,000 kg [1], but only 263 kg is in the surface environment such as atmosphere, hydrosphere and biosphere. In these surface reservoirs, more than 90% of the iodine (both ^{129}I and ^{127}I) exists in the ocean and sediments [1], the ocean is therefore considered as the main source of iodine in the atmosphere and biosphere.

Some investigations on the natural level of ^{129}I, as $^{129}\text{I}/^{127}\text{I}$ ratio, have been carried out by analyzing some samples collected before human nuclear activities or isolated environment in the past decades (Table 1). In groundwater, $^{129}\text{I}/^{127}\text{I}$ ratios of $(3\text{–}200)\times10^{-12}$ have been reported [2]. The varied values of $^{129}\text{I}/^{127}\text{I}$ might be attributed to the different sources of ^{129}I, besides the initially generated ^{129}I through cosmic ray reactions in the atmosphere and its deposition to the earth surface, migration of ^{129}I from surrounding environment containing high uranium which generated relative high amount of ^{129}I might be a reason of high ^{129}I level in some ground water samples. The high $^{129}\text{I}/^{127}\text{I}$ ratio in the ground water from the Stripa granite was interpreted as the injection of fission produced ^{129}I from the abundant ^{238}U in the granite matrix. $^{129}\text{I}/^{127}\text{I}$ ratios of $(5.7\text{–}165)\times10^{-12}$ in soil samples and $(4.6\text{–}1540)\times10^{-12}$ in animal thyroid samples collected before human nuclear activities during 1910–1947 have been reported [3]. This large variation in the $^{129}\text{I}/^{127}\text{I}$ ratios might attribute to two reasons: contamination of sample by anthropogenic ^{129}I during their storage and preparation for analysis; and the analytical methods employed in the earlier time were not reliable for low level ^{129}I samples with $^{129}\text{I}/^{127}\text{I}$ ratio lower than 10^{-10}. Up to date, no reliable value of the initial $^{129}\text{I}/^{127}\text{I}$ ratio in terrestrial environment is available. Although a value of 30×10^{-12} for $^{129}\text{I}/^{127}\text{I}$ ratio was observed in the seaweed collected in 1942, most of other analysis of marine samples, such as marine sediment, deep seawater has shown a constant $^{129}\text{I}/^{127}\text{I}$ ratio of $(1\text{–}2)\times10^{-12}$ [4–6], and a value of $(1.50\pm0.15)\times10^{-12}$ has been proposed as the initial value of $^{129}\text{I}/^{127}\text{I}$ in marine system without anthropogenic contribution [7].

The human nuclear activities since 1945 have released large amounts of fission products including ^{129}I to the environment. Among them the European nuclear fuel reprocessing plants are the major sources of ^{129}I, contributing more than 90% of the total inventory of ^{129}I in the present environment (Fig. 1), which includes the most important commercial reprocessing facilities at Sellafield (UK)

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Table 1
$^{129}I/^{127}I$ ratios reported in various environmental samples.

Type of sample	Sampling location	$^{129}I/^{127}I$, $\times 10^{-12}$ at/at	References
Pre-nuclear samples			
Ground water	Great Artesian Basin, Australia	~0.4–7.0	[8]
	Sweden (from granite)	3–200	[2]
Crustal fluids	Northeastern Bavaria	3.5	[9]
Sediment	continental slope in Atlantic Ocean	1.1–1.5	[4]
Seawater	the Gulf of Mexico	1.4	[10]
Seaweed	Japan	3–30	[11]
Fluids	Central American, volcanic Arc	0.5–0.8	[12]
Loess (deep layers)	XiFeng, China	~20	[13]
Human thyroid	U.S.A.	40	[14]
Thyroid powder	U.S.A.	7.0	[15]
Contaminated samples			
Seaweed	Near La Hague NFRP, France	~1,000,000	[16]
	North Sea	10,000–1,000,000	[17]
	Arctic ocean	1000–10,000	
Precipitation	Vicinity of the NFRP, Japan	11,000–5,000,000	[18]
Surface soil		3000–300,000	
Pine needles		370,000–18,000,000	
Algae		~1000	
Human thyroid	Gomel, Belarus	2650–11,000	[19]
Sheep thyroid	Ribe, Denmark	52,800–411,000	
Less contaminated samples			
Surface soil	Xi'an, China	453–1140	[13]
Coral	Zhanjiang, China	48.3	
Seawater	Near the NFRP, China	~100	[20]
Loess (shallow layers)	XiFeng, China	73–155	
	Xi'an, China	~42.0	
Snowmelt	Antarctica	44.7–86.1	[21]
River or lake water	Sungei Buloh Park	27.6	
	Singapore	86.4	
	Santiago, Chile	65.6	
	Iguaz Falls, Brazil	18.0	
Rain water	Xi'an, China	3260–3690	[20]

and La Hague (France), and approximately 75% of the discharges came from the latter one [22,23]. ^{129}I was released from these two reprocessing plants to both atmosphere and seas.

Iodine has a relative long residence time in the atmosphere (12–30 days depending on the species of iodine), and an even extremely long residence time in the ocean (40,000 y) due to its high solubility in seawater, and very slow removal process by biological particles [24]. The anthropogenic ^{129}I has been spread to large area, $^{129}I/^{127}I$ ratios in the environment have been risen up by several orders of magnitude compared to the level in pre-nuclear age (Table 1). In the highly contaminated areas, such as the environment in Europe, $^{129}I/^{127}I$ ratios of 10^{-6} in seawater and rainwater have been observed [25]; especially in the heavily contaminated locations such as the surrounding area of nuclear reprocessing plant, $^{129}I/^{127}I$ ratios as high as 10^{-4} in grass and animal thyroid have been reported. In the regions which were not exposed to direct contamination, such as in most of locations in China, $^{129}I/^{127}I$ ratios in surface soil, rainwater and coral, are at 10^{-10}-10^{-9}. This is mainly attributed to the global fallout of the atmospheric weapons testing in 1950s–1970s and possible dispersion of reprocessing released ^{129}I. This value can be considered as the natural background level at present time.

The high solubility of iodine in water and its easy transferring among different environmental media, as well as the long half-life (15.7 Ma) make ^{129}I well suited to many applications, such as tracing the movement and exchange of water masses in the seas [17,26], risk assessment of human exposure to the hazardous radioactive isotopes of iodine [19,27], tracing the migration of organic matter and age dating of the marine geological events between 2 and 80 Ma [7,9,28,29]. However, application of ^{129}I in geological dating of the terrestrial events is less investigated due to the difficulties in the analysis of terrestrial samples of low level iodine and ultra low level ^{129}I. Although many analytical methods has been reported for determination of ^{129}I, the determination of ultra low level ^{129}I in low iodine content samples is still a challenge, and method for speciation analysis of ^{129}I is still limited.

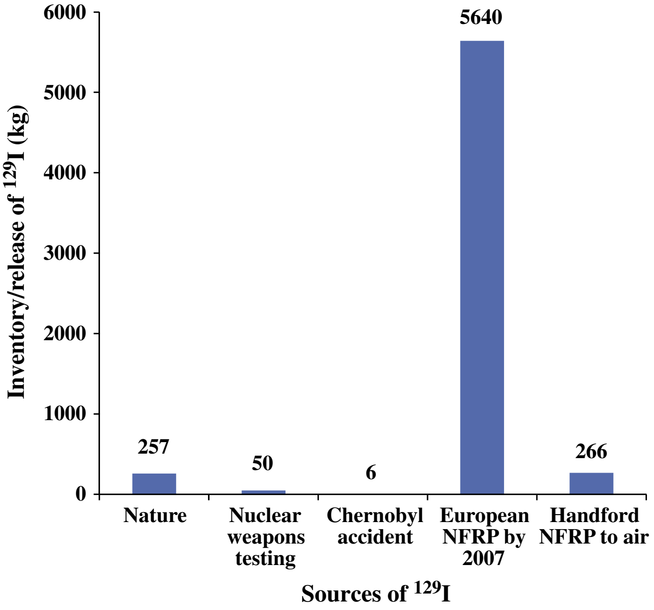

Fig. 1. Sources and inventories/releases of ^{129}I in the environment [23].

^{129}I is becoming an important radionuclide in environmental and geological researches due to its specific source term, as well as chemical, physical and environmental behaviors. In the past two decades, with the development of AMS technique and increased numbers of AMS facilities to be available for ^{129}I measurement, application of ^{129}I in geological and environmental researches has become more popular. While few review papers on ^{129}I have been published, especially on its application in geological and environmental researches. This article aims to overview the analytical methods for determination of ^{129}I, and major applications of ^{129}I in environmental and geological researches, and focus on the present progress and new findings.

2. Analytical techniques for ^{129}I

The concentration of ^{129}I in the environmental and geological samples is normally very low ($<10^{-10}$ g/g for solid samples, or $<10^{-12}$ g/L for water samples), iodine has to be first separated and pre-concentrated from the sample matrices and purified from interferences before measurement. A separation method with high iodine recovery and sufficient decontamination from interferences is the key point to obtain reliable analytical results.

2.1. Measurements of ^{129}I

^{129}I is a beta emitter with low energy gamma rays and X-rays emission. It can therefore be measured by radiometric methods, such as gamma or X-ray spectrometry, and liquid scintillation counting. Due to the long half life of ^{129}I, the analytical sensitivity of radiometric is not high. To obtain a sufficient sensitivity, neutron activation analysis (NAA) has been used by converting ^{129}I to short-lived ^{130}I which is measured by gamma spectrometry. In the recent years, inductively