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Development of a Method for ^{129}I Determination Using Radiochemical Neutron Activation Analysis

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Abstract

In this work an RNAA method for ^{129}I determination was developed. The decomposition of the samples (up to 150 g of soil or plant material) was made by alkaline fusion, where the ratio of sample: KOH and the heating conditions were crucial. The sample was then leached with water and then neutralised with H_2SO_4 (96%). The iodine present in the leachate was oxidised by the addition of $NaNO_2$ (10%) and H_2SO_4 (2.5 mol L^{-1}) and extracted into chloroform, followed by the reduction and stripping of iodine with Na_2SO_3 (10%) into an aqueous phase. Iodine was again oxidised, purged from the system with nitrogen and adsorbed onto activated charcoal. We optimised the flow rate of nitrogen, the duration of the process, the amount of charcoal needed to trap iodine and improved the purity of the charcoal, because its chemical composition (traces of K, Na, Br) influences the activity levels (dose rate) of the irradiated charcoal and prolongs the cooling time required before the radiochemical separation of the radioisotope ^{130}I, induced by the nuclear reaction ^{129}I(n,γ)^{130}I ($t_{½}$ = 12.36 h, E_γ = 536 keV), can be made. The chemical yield for the whole procedure was determined spectrophotometrically and via the nuclear reaction ^{127}I(n,2n)^{126}I.

The method was developed, optimised and validated using the reference material IAEA-375 Soil and a good agreement between the obtained and recommended values was found. The measurement uncertainty of the method was also assessed. The method developed was used to investigate the content of ^{129}I in brown algae (*Fucus virsoides*) collected along the Slovene coast and the results found were in the order of 4×10^{-7} μg g^{-1}.

Keywords: ^{129}I, RNAA, IAEA-375 Soil, measurement uncertainty, brown marine algae

1. Introduction

^{129}I is a long-lived ($t_{½}$ = 1.57×10^7 y) naturally occurring radioisotope whose environmental abundance has been changed by man mainly due to emissions from nuclear fuel reprocessing plants. The greatest releases of ^{129}I were from two European reprocessing plants located at La Hague (France) and Sellafield (England). The solubility of iodine in water, its high volatility and long residence time makes ^{129}I an ideal environmental tracer, and a source of radiological concern.[1]

Only accelerator mass spectrometry (AMS) is sensitive enough to determine the pre-nuclear levels of ^{129}I in environmental samples. The ratio of ^{129}I/^{127}I in the marine environment has increased to $10^{-11} - 2 \times 10^{-10}$ and in the terrestrial environment to $10^{-9} - 10^{-7}$. The detection limit of radiochemical neutron activation analysis (RNAA) expressed as the ^{129}I/^{127}I ratio is $10^{-10} - 10^{-12}$, which is sensitive enough to determine ^{129}I in todays environmental samples.[2,3]

The concentration levels of ^{129}I in environmental samples are very low and chemical separation/pre-concentration procedures have to be developed which can be used for a wide variety of matrices. Combustion methods are commonly used for sample preparation for RNAA. Schmidt et al.[2] heated the sample material (70 g of soil) in a stream of oxygen and nitrogen, first at 600–1000 °C and then at a temperature of 1100 °C. The evaporated iodine was absorbed on an activated charcoal trap and after post-irradiation chemistry the iodine was precipitated as AgI and measured by γ-spectrometry. ^{125}I was added for the chemical yield determination.

Hou et al.[3] used alkaline leaching with KOH (10 g) for pre-concentration of iodine from soil samples (3–5 g) and they added ^{125}I solution for chemical yield determination. After leaching, iodine was separated by an extraction (CCl_4) and back-extraction cycle. LiOH was added and the back-extracted aqueous phase was transferred to a quartz ampoule and dried at 70–80 °C. After post-irradiation purification of iodine, $PdCl_2$ solution was added to precipitate iodine as PdI_2, which was then measured by γ-spectrometry.

Quintana et al.[4] used digestion by alkaline fusion with KOH to determine ^{129}I in conifer samples. ^{131}I was added as a tracer to determine the chemical yield. They purified iodine before irradiation by distillation, followed by solvent extraction and adsorption on activated charcoal during redistillation. After irradiation radiochemical purification by distillation was performed, followed by solvent extraction and γ-spectrometry of the purified aqueous phase.

The aim of this work was to develop a simple and rapid RNAA method capable of determining ^{129}I at ultra trace levels using the Ljubljana 250 kW TRIGA Mark II reactor at the relatively modest thermal fluence rate of 3.5×10^{12} n cm^{-2} s^{-1}. We wanted to use as great a sample mass as possible for the pre-concentration of ^{129}I on to a small amount of active charcoal of high purity, followed by combustion in an oxygen atmosphere of the irradiated charcoal and then extraction of I_2 with $CHCl_3$ using classical redox reactions with $NaNO_2$ and Na_2SO_3 in H_2SO_4 medium. Furthermore, we wished to apply the method to determine ^{129}I in the brown algae *Fucus virsoides* collected along the Slovene coast, because no data for ^{129}I in seaweeds from the Adriatic Sea have been reported. Brown algae are known to accumulate iodine and some other elements (and radionuclides) in high concentrations and are used as marine monitors for radionuclide discharges from the Sellafield and La Hague reprocessing plants.[5]

2. Experimental

2. 1. Samples

The method was developed and validated using the reference material IAEA-375 (Radionuclides and Trace Elements in Soil). This reference material is intended to use as a quality control material for the assessment and validation of analytical methods, and for quality assurance within a laboratory.[6]

The method was applied to determine the content of ^{129}I in the brown algae *Fucus virsoides* collected along the coast of Slovenia. Algae were dried with freeze dryer (Christ Alpha 1-4, LOC-1, Germany) at –54° C for 172 hours to constant mass.

2. 2. ^{131}I tracer Preparation

^{131}I ($t_{½}$ = 8.02070 d, E_{γ} = 364.5 keV) was provided monthly from the Department of Nuclear Medicine (Clinical Centre Ljubljana, Slovenia). After use of ^{131}I for therapy of the thyroid gland, the used, empty bottles contain enough ^{131}I to prepare a working ^{131}I tracer solution (count rate ~1–2 cps).

2. 3. Pre-concentration of Iodine

The IAEA-375 Soil sample (100–150 g) was decomposed by alkaline fusion in 300 g of KOH. Iodine carrier (150–200 mg of a solution of KI in NH_3 containing 50 mg I g^{-1} in a 5% solution of ammonia) to assure reproducible conditions and to determine the chemical yield and 30–50 mL of water were added to the sample. The decomposition was performed in a nickel crucible, which was placed in an oven at 70–80 °C to dry the sample for about 24 h. The sample was then gradually heated, first on a heating block to 350 °C and then in a muffle furnace to 600 °C and maintained at this temperature for 4 h. After cooling, the iodine in the alkaline residue was then leached with hot water and reduced by the addition of 5 mL of Na_2SO_3 (10%) and the leachate was neutralised with concentrated H_2SO_4 (96%). The neutralized leachate was transferred to a separation funnel and iodine oxidised by the addition of 5 mL of $NaNO_2$ (10%) and 3 mL of H_2SO_4 (2.5 mol L^{-1}) and extracted into $CHCl_3$. Iodine was then reduced with Na_2SO_3 and purged from the aqueous phase with nitrogen and trapped on 250 mg of purified activated charcoal.

2. 4. ^{129}I/^{127}I Standard Preparation

A working standard solution of $^{129}I/^{127}I$ (A = 4.2 Bq g^{-1}) was prepared by dilution of an original ^{129}I standard solution (LEA Cerca, A = 420 Bq g^{-1}) with 0.3% LiOH. Potassium iodide as a source of stable ^{127}I was added. The prepared $^{129}I/^{127}I$ standard contained 50 mg g^{-1} ^{127}I and 0.63 μg g^{-1} of ^{129}I. From the thus prepared $^{129}I/^{127}I$ working standard solution, approximately 100 – 150 mg were added to a quartz ampoule and dried at 60 °C.

2. 5. Irradiation of Sample and Standard

The activated charcoal was sealed in a quartz ampoule and irradiated simultaneously with the $^{129}I/^{127}I$ standard in the F ring (channels F15 and F19) of the Ljubljana TRIGA Mark II reactor at a thermal neutron fluence rate of 3.5×10^{12} n cm^{-2} s^{-1} and fast neutron fluence rate of 1.2×10^{12} n cm^{-2} s^{-1} (thermal to fast ratio is 3 : 1) for 12 h. After the nuclear reactions $^{129}I(n,\gamma)^{130}I$ (σ_{th} = 27 b, $t_{½}$ = 12.36 h, E_{γ} = 536 keV) and $^{127}I(n,2n)^{126}I$ (σ_f = 0.9 b, $t_{½}$ = 13 d, E_{γ} = 389 keV) occurring with thermal and fast neutrons, respectively, ^{130}I and ^{126}I may be determined simultaneously from the same γ-spectrum, following radiochemical separation.

2. 6. Radiochemical Separation and Measurement of γ-activity of ^{130}I and ^{126}I

After about 10–12 hours cooling, the irradiated activated charcoal was combusted in an oxygen atmosphere (4L Schöniger flask) containing a reducing acid solution, followed by extraction of iodine with $CHCl_3$ after oxidation with $NaNO_2$ (10%). Reductive stripping of the organic phase with Na_2SO_3 (10%) to purify iodine from bromine followed. Iodine was then re-extracted with $CHCl_3$ after oxidation and transferred to a vial for gamma-ray measurement (coaxial type HPGe detector) of the induced radioisotopes ^{126}I and ^{130}I from the sample.

The ampoule containing the $^{129}I/^{127}I$ standard was carefully cut with a knife and the iodine was leached from the ampoule with NaOH solution (1 mol L^{-1}) and Na_2SO_3 solution (10%). The leachate was transferred to a separation funnel and the iodine was separated by extraction described above. The recovery for iodine from the working standard solution, determined spectrophotometrically, for each aliquot, was in the range of 85–90%.

2. 7. Determination of Stable Iodine ^{127}I

The method for stable iodine determination by RNAA was based on simultaneous irradiation of the sample (a pelletized mixture of soil (180 mg) and cellulose powder (120 mg)) and a standard solution (prepared from a working solution of 100 µg of 10 µg I g^{-1} in a 5% solution of NH_3) sealed in a polythene ampoule, for approximately 1 minute in a rabbit in the pneumatic tube (PT) of the TRIGA Mark II reactor at a thermal neutron fluence rate of about 3.5×10^{12} n cm^{-2} s^{-1}. The PT is also situated in the F ring in position F24 and the irradiation conditions are very similar to those in channel F15 and F19. The irradiated sample and 90–100 mg of iodine carrier (solution of KI in NH_3; 50 mg I g^{-1} in 5% solution of NH_3) were then combusted in an oxygen atmosphere (4L Schöniger flask), followed by absorption of iodine in a reducing acid solution and extraction of iodine with $CHCl_3$ via the classical redox reaction with $NaNO_2$. Stripping of the organic phase to purify iodine followed, which was then re-extracted with $CHCl_3$ and transferred to a vial for gamma-ray measurement of the induced radionuclide ($^{127}I(n,\gamma)^{128}I$, σ_{th} = 6.2 b, $t_{½}$ = 25 min, E_γ = 442.9 keV).[7–9]

After gamma-ray measurement, the organic phase was quantitatively transferred to a flask for spectrophotometric chemical yield determination of iodine at 517 nm.

3. Results and Discussion

3.1. Pre-concentration

The optimal conditions for the pre-concentration of iodine from the sample were investigated using ^{131}I as a tracer, making use of the fact that the chemical properties of different isotopes of an element are the same. Two pre-

Table 1: Results and optimal conditions for pre-concentration and trapping of iodine from IAEA-375 Soil.

Parameters	Range	Yield η (%)	Optimal conditions
ratio sample:KOH	1:2	40 ± 7	
	1:3	87 ± 5	**1:3**
	1:4	88 ± 5	
decomposition conditions	oven:		
	25 °C, 24 h		
	70–80 °C, 24 h		70–80 °C, 24 h
	70–80 °C, 48 h		
	heating block:		
			150 °C, 12 h
	100–350 °C, 24–60 h		240 °C, 24 h
			350 °C, 12 h
	muffle furnace:		
	560 °C, 4 h	72 ± 4	600 °C, 4 h
	600 °C, 4 h	87 ± 5	
flow rate of nitrogen (mL/min)	8	70 ± 5	
	10	85 ± 4	
	12	97 ± 2	12
	15	89 ± 6	
influence of the amount of activated charcoal on chemical yield	amount (mg)		
	100	70 ± 5	
	150	81 ± 4	
	200	89 ± 2	250
	250	97 ± 2	
	300	97 ± 2	
Duration of trapping process (min)	45	80 ± 5	
	60	97 ± 2	60
	75	93 ± 5	

concentration procedures were investigated: cycling combustion in a Schöniger flask and alkaline fusion.

The main disadvantage of combustion in a Schöniger flask is the limitation of the amount of sample that can be combusted. In one single step approximately 500 mg of sample can be ignited. Therefore we tried the so-called cycling combustion method where we simply repeated the combustion in the same Schöniger flask twenty times and the total amount of the sample reached with this method was 10 g. The iodine evaporated from the ignited sample was trapped in a reducing solution in the Schöniger flask containing Na_2SO_3 (10%) and H_2SO_4 (0.05 M). Iodine was then oxidised by the addition of $NaNO_2$ and purged from the medium with nitrogen and trapped on activated charcoal. Various flow rates of nitrogen and durations of the process were investigated in order to optimise the recovery of iodine, but the chemical yields never exceeded 50%.

In searching for the optimal conditions for pre-concentration of iodine by alkaline fusion, 10 g of IAEA-375 Soil sample was processed. We decided to use this matrix because it is difficult to digest due to silicates present (typically content of Si is around 20%). The ratio between sample and KOH and the decomposition conditions were investigated and the results obtained are summarised in Table 1.

The main advantage of alkaline fusion in KOH was the amount of sample which could be processed (up to 150 g). After alkaline fusion was performed the residue was leached with hot water and neutralized with concentrated H_2SO_4.

We attempted to purge iodine directly from the neutralised residue with nitrogen and the influence of possi-

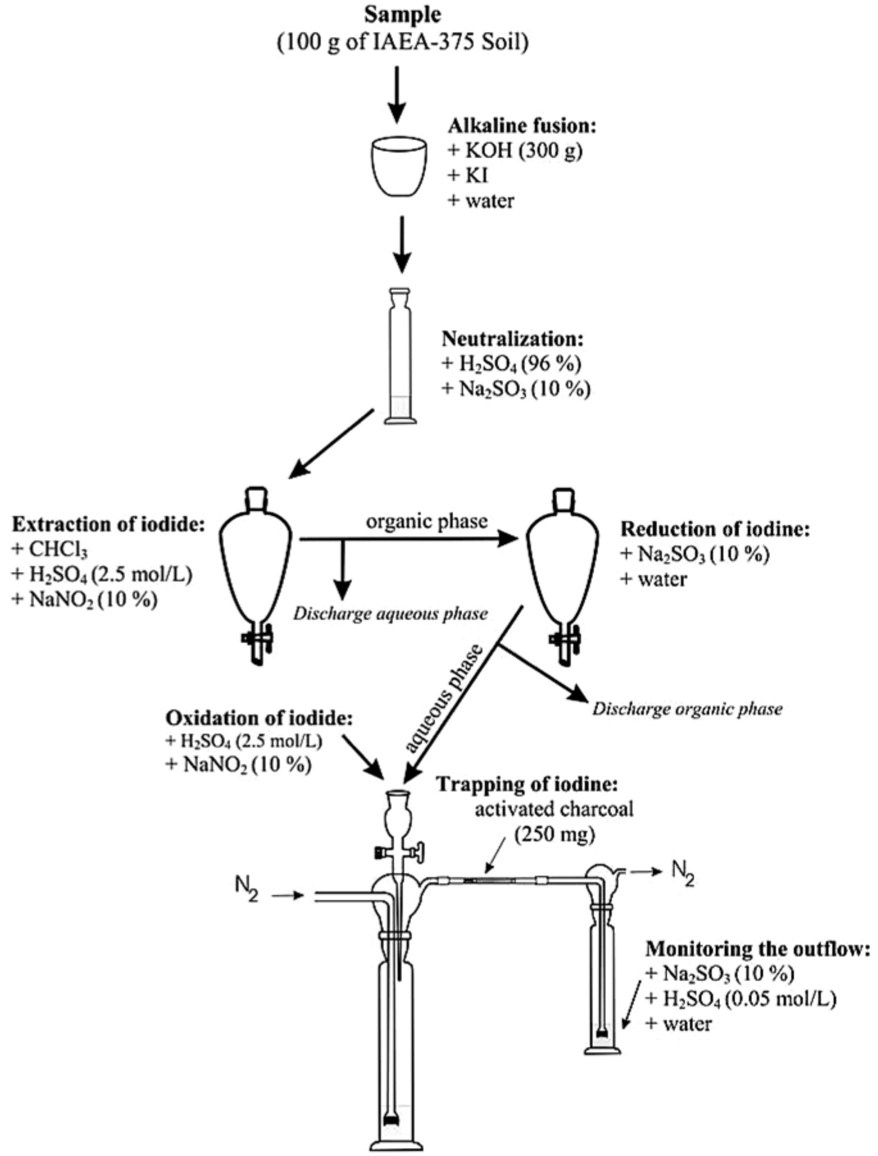

Figure 1: The scheme for pre-concentration of iodine from IAEA-375 Soil

Table 2: Chemical composition of activated charcoals obtained by k_0-INAA

	Merck 9624	**Merck 2514**	**Sigma Darco 242241**	**BDH**
Element	**Content (µg/g)**			
Ag	< 0.26	< 0.20	< 0.27	< 0.29
As	7.70 ± 0.28	2.82 ± 0.10	11.00 ± 0.40	24.70 ± 0.90
Au	< 0.001	< 0.001	0.006 ± 0.0003	< 0.001
Ba	99.4 ± 4.9	38.1 ± 1.7	502.0 ± 18.0	287.0 ± 10.0
Br	< 0.29	1.47 ± 0.07	2.70 ± 0.10	3.33 ± 0.16
Ca	1500 ± 203	< 938	1553 ± 199	3157 ± 249
Cd	< 0.54	< 0.60	< 1.06	< 0.71
Ce	14.70 ± 0.50	4.56 ± 0.17	6.64 ± 0.30	10.90 ± 0.40
Co	19.20 ± 0.70	5.86 ± 0.21	4.64 ± 0.16	5.40 ± 0.21
Cr	12.0 ± 0.5	11.2 ± 0.4	17.7 ± 0.8	18.7 ± 0.7
Cs	0.53 ± 0.02	0.33 ± 0.01	0.22 ± 0.02	0.23 ± 0.01
Cu	< 50	< 50	< 259	< 101
Eu	0.42 ± 0.03	0.12 ± 0.01	0.14 ± 0.02	0.29 ± 0.03
Fe	3893 ± 138	936 ± 33	1490 ± 53	16904 ± 592
Ga	5.66 ± 0.30	6.15 ± 0.22	9.03 ± 0.83	2.94 ± 0.36
Hf	0.51 ± 0.02	0.42 ± 0.02	1.95 ± 0.07	< 0.32
Hg	< 0.07	< 0.40	< 0.32	< 0.07
In	< 0.43	< 0.40	< 0.40	< 0.49
K	1110 ± 47	578 ± 21	518 ± 92	819 ± 64
La	6.90 ± 0.24	2.69 ± 0.09	3.63 ± 0.13	6.09 ± 0.22
Mo	2.30 ± 0.17	2.24 ± 0.07	13.30 ± 0.70	4.60 ± 0.19
Na	486 ± 17	285 ± 10	2562 ± 90	1975 ± 69
Nd	8.30 ± 0.48	2.46 ± 0.21	3.51 ± 0.46	5.65 ± 0.47
Rb	6.84 ± 0.36	4.16 ± 0.20	2.23 ± 0.26	4.55 ± 0.36
Sb	1.97 ± 0.07	1.46 ± 0.05	3.79 ± 0.14	1.67 ± 0.06
Sc	3.86 ± 0.14	1.23 ± 0.05	4.81 ± 0.17	2.62 ± 0.09
Se	3.09 ± 0.13	3.07 ± 0.12	34.20 ± 1.20	1.97 ± 0.10
Sm	1.77 ± 0.07	0.47 ± 0.02	0.65 ± 0.03	1.25 ± 0.07
Sr	130.0 ± 6.0	36.6 ± 3.8	107.0 ± 7.0	177.0 ± 8.0
Ta	0.130 ± 0.010	0.115 ± 0.006	0.330 ± 0.010	0.08 ± 0.01
Tb	0.300 ± 0.010	0.077 ± 0.004	0.125 ± 0.006	0.180 ± 0.010
Te	< 0.10	< 0.20	< 0.10	< 0.10
Th	1.92 ± 0.07	0.74 ± 0.03	5.73 ± 0.20	1.36 ± 0.05
U	1.50 ± 0.05	1.16 ± 0.04	5.73 ± 0.21	0.51 ± 0.02
W	0.81 ± 0.05	1.42 ± 0.05	2.61 ± 0.14	0.69 ± 0.15
Yb	1.13 ± 0.06	0.26 ± 0.01	0.59 ± 0.03	0.42 ± 0.02
Zn	< 1.80	< 0.40	1.38 ± 0.30	24.30 ± 1.00
Zr	< 24.0	< 25.0	81.4 ± 9.5	< 19.0

ble interfering elements (As, Br, Cl and Sb) from the sample matrix on the selectivity for trapping of iodine on activated charcoal was investigated. Carrier solutions of As (50 mg As g^{-1}, aqueous solution of As_2O_3), Sb (50 mg Sb g^{-1}, solution of Sb_2O_3 in 2 mol L^{-1} HCl), Cl (60 mg Cl g^{-1}, aqueous solution of NaCl), Br (60 mg Br g^{-1}, aqueous solution of NaBr) and tracer solutions of ^{76}As (10 µg As g^{-1}, $^{75}\mathrm{As}(n,\gamma)^{76}\mathrm{As}$, 559.1 keV), ^{122}Sb (20 µg Sb g^{-1}, $^{121}\mathrm{Sb}(n,\gamma)^{122}\mathrm{Sb}$, 564.1 keV), ^{38}Cl (50 µg Cl g^{-1}, $^{37}\mathrm{Cl}(n,\gamma)^{38}\mathrm{Cl}$, 1642.4 keV) and ^{82}Br (20 µg Br g^{-1}, $^{81}\mathrm{Br}(n,\gamma)^{82}\mathrm{Br}$, 776.5 keV) were prepared from the same chemicals. Each carrier (100 mg) and tracer (30 mg) solution was added separately to a reducing solution (25 mL 0.05 M H_2SO_4 + 5 mL 10% Na_2SO_3) containing 100 mg of iodine carrier (50 mg I g^{-1}) and 30 mg of working ^{131}I tracer solution. For As, Sb and Cl no interference was observed; these elements were not adsorbed on the charcoal, and 98 ± 1% of added ^{131}I was adsorbed. Only in the case of bromine was 1–2% of added Br (20 µg g^{-1}) adsorbed on the activated charcoal, but with no effect on adsorption of ^{131}I (97 ± 2%).

However, the direct method of adsorbing iodine on activated charcoal was not practical, because the neutralised leachate (mainly K_2SO_4) was too dense. Therefore we transferred it to a separating funnel and iodine was oxidised with $NaNO_2/H_2SO_4$ and extracted with $CHCl_3$. Back-extraction of iodine with Na_2SO_3 into the aqueous phase followed, which was collected and the iodide was then reoxidised by $NaNO_2$, purged from the aqueous phase with nitrogen and adsorbed onto activated charcoal (Figure 1).

3. 2. Trapping of Iodine

Trapping of iodine on activated charcoal was necessary because of the limitation on the amount of sample that can be irradiated (the size of rabbits for irradiation), and it is preferable to irradiate samples in solid form (formation of radiolytic gases and the increase of pressure are reduced). The maximum temperature reached in the F ring of the TRIGA Mark II reactor is up to 60 °C, and we found no losses (desorption) of iodine from the charcoal during irradiation.

To evaluate possible losses of iodine from the ^{129}I/^{127}I standard solution during drying, a tracer experiment with a working ^{131}I tracer solution was performed, but no losses were observed.

3. 3. Characteristics of Charcoal Used

The elements present in charcoal influence its activity after irradiation, so cooling time is necessary to reduce the exposure levels to the safe range (ALARA principle) before starting the radiochemical separation of ^{129}I. To find an appropriate charcoal, the concentrations of various elements present in charcoals from different producers were determined by k_0-INAA.[10] The results are shown in Table 2. The induced activity levels are mainly due to the radioisotopes ^{23}Na(n,γ)^{24}Na ($t_{1/2}$ = 14.96 h), ^{41}K(n,γ)^{42}K ($t_{1/2}$ = 12.36 h) and ^{81}Br(n,γ)^{82}Br ($t_{1/2}$ = 35.30 h) from traces of sodium, potassium and bromine present in the activated charcoal. Sigma Darco® and BDH have too high sodium contents and of the two remaining charcoals, MERCK 9624 charcoal has no bromine and a favourable granulation in comparison to MERCK 2514 charcoal. Hence we selected MERCK 9624 (Darmstadt) charcoal for adsorbing iodine.

The charcoal selected also contained traces of uranium and caesium (Table 2), which can cause interfering and undesired nuclear reactions in the determination of ^{129}I, as follows: ^{235}U(n,f)^{131}I, ^{235}U(n,f)^{133}I, ^{235}U(n, f)^{129}I (n,γ)^{130}I, ^{235}U(n,f)^{130}I and ^{133}Cs(n,α)^{130}I.[3,9]

To minimise its uranium and caesium content, MERCK 9624 charcoal was cleaned using different acids; HCl (1–6 mol L^{-1}), HNO$_3$ (1–14 mol L^{-1}) and CH$_3$COOH (1–16 mol L^{-1}). For this experiment 30 mL of acid were added to 2 g of charcoal and shaken for 24 h. The charcoal

Table 3: Results of cleaning Merck 9624 charcoal by different procedures, obtained by k_0-INAA

Treatment		**Element concentration (µg/g)**				
		Br	**K**	**Na**	**Cs**	**U**
No treatment		< 0.25	1110 ± 47	486 ± 17	0.53 ± 0.02	1.50 ± 0.05
Acid	**C (mol L^{-1})**					
HCl	1	1.68 ± 0.06	1290 ± 179*	422 ± 15*	0.60 ± 0.03*	0.69 ± 0.02
	2	2.13 ± 0.08				0.66 ± 0.03
	3	2.43 ± 0.09				0.72 ± 0.03
	4	2.89 ± 0.10				0.83 ± 0.03
	5	3.05 ± 0.11				0.97 ± 0.04
	6	3.74 ± 0.14				1.10 ± 0.05
	9	16.2 ± 0.6				0.69 ± 0.03
HNO$_3$	1	< 0.25	1070 ± 58*	385 ± 14*	0.54 ± 0.02*	0.80 ± 0.03
	3	< 0.25				0.76 ± 0.03
	6	0.34 ± 0.05				0.65 ± 0.02
	8	0.30 ± 0.05				0.65 ± 0.02
	10	0.53 ± 0.02				0.60 ± 0.02
	12	0.27 ± 0.02				0.61 ± 0.02
	14	0.84 ± 0.04				0.63 ± 0.02
CH$_3$-COOH	1	0.60 ± 0.03	1203 ± 71*	423 ± 15*	0.60 ± 0.03*	1.57 ± 0.06
	2	1.35 ± 0.05				1.54 ± 0.06
	4	0.72 ± 0.03				1.48 ± 0.05
	6	0.60 ± 0.03				1.39 ± 0.05
	8	0.25 ± 0.03				1.33 ± 0.05
	10	0.35 ± 0.03				1.30 ± 0.05
	12	0.31 ± 0.03				1.26 ± 0.05
	14	0.55 ± 0.03				1.32 ± 0.06
	16	0.65 ± 0.03				1.37 ± 0.05
Heating at 900 °C		< 0.25	1185 ± 45	446 ± 16	0.58 ± 0.02	1.48 ± 0.05
HCl/Aqua regia		3.74 ± 0.13	1165 ± 61	351 ± 13	0.55 ± 0.03	0.54 ± 0.02

*Average value; the effect of different acid concentrations used was not appreciable.

was then washed several times with water to remove any acid residues and then dried at 110 °C (Table 3).

Activated charcoal was also cleaned by heating in a nitrogen atmosphere at 900 °C and by using a preparation procedure described by Izgi and coauthors.[11] In the first stage activated charcoal was treated with concentrated hydrochloric acid and boiled for 3 h with stirring, then washed and dried. In the second stage of the cleaning procedure it was treated with aqua regia ($HCl–HNO_3$, 3 : 1) for 24 h with stirring, then filtered, washed and dried at 110 °C. The elemental content in the purified charcoal is presented in Table 3.

To evaluate the interferences of nuclear reactions, blank samples of activated, cleaned charcoal were irradiated in the central channel and in the F ring (two positions – F15 and F19) of the TRIGA Mark II reactor, then processed as described under Experimental – section 6, and measured on a well type HPGe detector. The formation of ^{130}I was below the detection limit and therefore the production of ^{130}I from uranium and caesium impurities is negligible for this method, but the formation of ^{133}I ($t_{½}$ = 20.8 h) and ^{131}I ($t_{½}$ = 8.02070 d) was observed (Table 4).

The preparation of the charcoal trap was also very important. We prepared the charcoal trap by weighing 250 mg of activated charcoal, then putting it into a quartz tube, sealing it with quartz wool and shaking the trap on a shaker (vortex) to achieve a homogeneous arrangement of the charcoal. The adsorption of iodine using ^{131}I tracer was in the range from 95–99%.

3. 4. Irradiation of Sample and Standard

Positions possible for irradiation of sample and standard at the TRIGA Mark II reactor are the F ring with a thermal neutron fluence rate of 3.5×10^{12} n cm^{-2} s^{-1} and fast neutron fluence rate of 1.2×10^{12} n cm^{-2} s^{-1}, and the central channel with thermal and fast neutron fluence rates of 1×10^{13} n cm^{-2} s^{-1}.

To find appropriate irradiation conditions the ALARA principle was followed. The fluence rate of thermal neutrons in the F ring was enough to induce the radionuclide ^{130}I via the $^{129}I(n,\gamma)^{130}I$ nuclear reaction and there was an important advantage in comparison to the central channel. Namely, the fluence rate of fast neutrons in the F ring is about three times lower than the fluence rate in the central channel. Also the reaction of stable iodine ^{127}I with fast neutrons via the $^{127}I(n,2n)^{126}I$ nuclear reaction is reduced and the activity of the induced ^{126}I ra-

Table 4: Radionuclides ^{133}I and ^{131}I induced from U present in irradiated, cleaned charcoal (irradiated for 12h)

Mass of charcoal (g)	**Measuring time (s)**	**^{131}I** Area counts	**^{133}I** Area counts	**^{131}I** Specific activity (s^{-1}g^{-1})	**^{133}I** Specific activity (s^{-1}g^{-1})	**^{133}I/^{131}I Ratio**
Central channel						
0.1692	2000	2289	29997	6.76	88.64	13.11
0.1754		2366	32057	6.75	91.38	13.54
0.1867		2492	33321	6.67	89.24	13.38
F ring (position F15)						
0.2498	36000	9115	125492	1.01	13.95	13.77
0.2532		9636	130752	1.06	14.34	13.57
0.2516		9416	127461	1.04	14.07	13.54
F ring (position F19)						
0.2568	36000	10008	137689	1.08	14.89	13.76
0.2487		12038	164012	1.34	18.32	13.62
0.2506		11940	157439	1.32	17.45	13.19

Table 5: Concentrations of ^{129}I and ^{127}I in IAEA-375 Soil

Reference	**^{129}I (10^{-7} µg g^{-1})**	**^{129}I (10^{-3} Bq kg^{-1})**	**^{127}I (µg g^{-1})**	**^{129}I/^{127}I (10^{-10})**
[6]	2.62 ± 0.81	1.71 ± 0.53 (0.8–2.6)[a]	1.91 ± 0.49	~1310
[2]	2.50 ± 0.70	1.60 ± 0.50	1.68 ± 0.09	1465
This work (n = 5)	3.05 ± 0.84	2.03 ± 0.56	1.73 ± 0.07	1760
Recommended value [12]		1.7 (1.3–2.1)[b]		

Results are given with measurement uncertainty (95% Confidence interval, k = 2)
[a] Range of accepted laboratory averages (n = 11) [b] 95% Confidence Interval (n = 10)

dionuclide then has less influence on the background of the measured γ spectrum.

After irradiation the samples were left to decay for 10–12 h, which was enough to reduce the exposure levels to the safe range (ALARA).

3. 5. Chemical Recovery

The use of ^{131}I and ^{125}I as tracers for chemical yield determination can be found in the literature.[2–4] Quintana et al.[4] preferred ^{131}I over ^{125}I because it allowed simultaneous determination of ^{130}I activity and of total recovery at the same time. When using ^{125}I it is necessary to cool the sample to eliminate the Compton radiation.[4]

The use of ^{131}I as a tracer for chemical yield determination was foreseen. We made an experiment to evaluate possible interferences from the ^{131}I(n,2n)^{130}I (σ_f = 80 b) nuclear reaction, because interferences from the activated charcoal itself on formation of ^{130}I were already shown to be negligible. Approximately 100 mg of the working ^{131}I tracer solution was adsorbed on 250 mg of activated charcoal and irradiated simultaneously with the ^{129}I/^{127}I standard in the central channel of the TRIGA Mark II reactor. Formation of ^{130}I, with an activity corresponding to 3.0×10^{-4} μg ^{129}I g^{-1} could be observed. The same experiment was also performed in the F ring of the reactor, but formation of ^{130}I was not observed in this case.

Thus the fluence rate of fast neutrons in the F ring of the reactor was not high enough to produce ^{130}I via the ^{131}I(n,2n)^{130}I nuclear reaction if using ^{131}I as a tracer. Due to residual U content in cleaned charcoal, the interfering nuclear reaction ^{235}U(n,f)^{131}I was observed after irradiation in the central channel and also in the F ring (Table 4), so chemical yield determination with ^{131}I was not directly possible. Quintana and Thysen used charcoal in the preconcentration process and determined the chemical yield using ^{131}I taking into account ^{131}I generated from U in charcoal, which in their case was about 4–6%,[4] but they did not discuss the elemental composition of charcoal and the interfering reaction ^{131}I(n,2n)^{130}I under their irradiation conditions.

In our procedure the chemical yield was determined both spectrophotometrically and by using the ^{126}I activity. The concentration of ^{127}I in the IAEA-375 Soil was taken into account when calculating the chemical yield. The destruction of IAEA-375 Soil by alkaline fusion yielded a chemical recovery for iodine of 70–80%. The post-irradiation step reduced the total yield to 60–70%. The detection limit for ^{129}I was 5×10^{-14} g g^{-1} sample.

The results for determination of ^{129}I and ^{127}I by RNAA in IAEA-375 Soil (the only commercially available reference material for ^{129}I) are presented in Table 5 and Figure 2, and compared to the IAEA recommended value and to values found in the literature. As shown, the agreement is excellent.

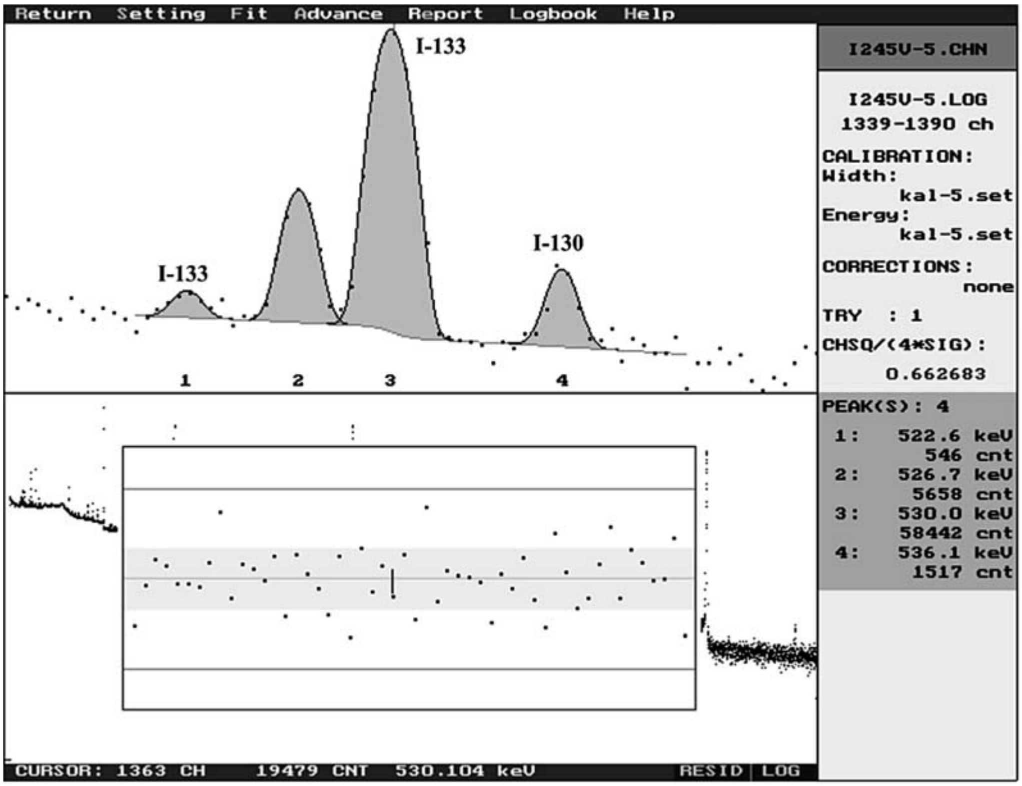

Figure 2: Gamma-spectrum of ^{130}I after pre-separation on charcoal and RNAA separation of IAEA 375 Soil

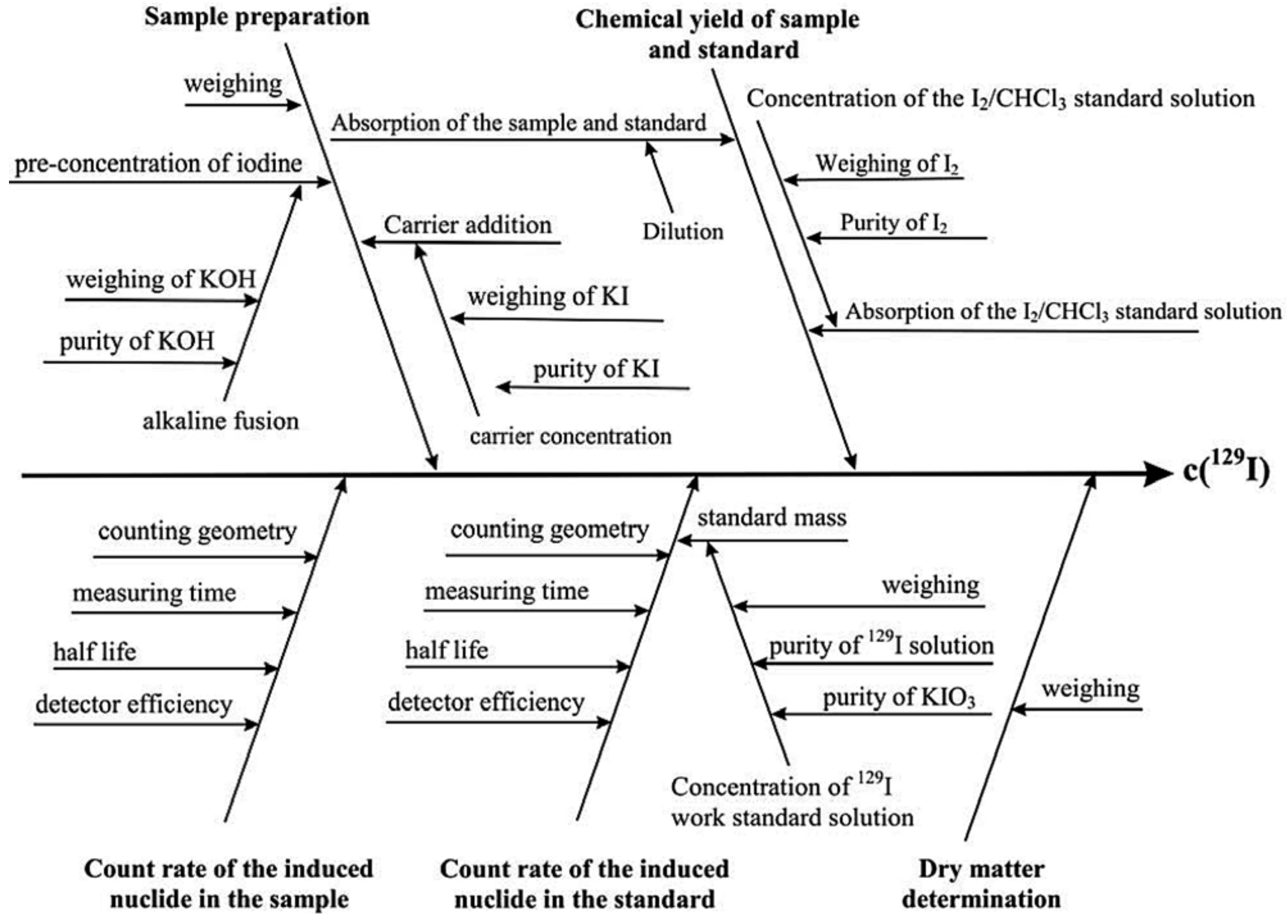

Figure 3: Sources of uncertainty in the determination of ^{129}I

3. 6. Measurement Uncertainty

An evaluation of measurement uncertainty for the determination of ^{129}I by the developed RNAA method was made. The uncertainty budget of measurement results was computed according to the principles prescribed by the ISO Guide to the Expression of Uncertainty in Measurement (GUM).[13]

The measurand was specified as the concentration of ^{129}I in the standard reference material (IAEA 375) Radionuclides and Trace Elements in Soil; c (^{129}I) [μg g^{-1}]. The main sources of uncertainty are presented in Figure 3 and they contributed 94% to the overall measurement uncertainty (Figure 4).

The major sources of uncertainty were found to be due to the repeatability of the chemical yield determination, the count rate of the induced nuclide in the ^{129}I/^{127}I working standard solution, the count rate of the induced nuclide in the sample and the certified uncertainty of the ^{129}I solution activity (Cerca Lea). The measurement uncertainty evaluated for determination of ^{129}I in IAEA 375 Soil is in good agreement with the measurement uncertainties found by Schmidt et al. and Strachnov et al., which are presented in Table 5.[2,6]

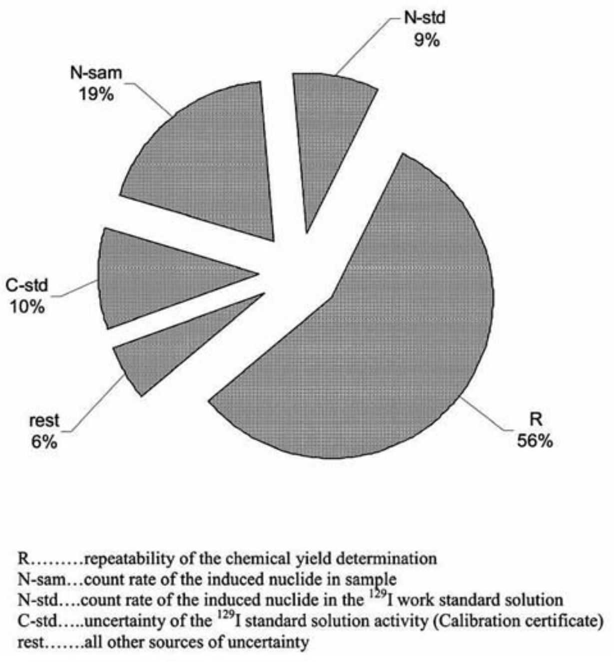

Figure 4: Contributions to the uncertainty budget for ^{129}I determination in standard reference material IAEA 375

The major uncertainty contributions found in this work are very similar to the uncertainty contributions found in our previous work.[9] There we evaluated the measurement uncertainty for the determination of iodine by a rapid RNAA method. We found that the repeatability of the chemical yield determination and the count rate of the induced nuclide in standard and sample contributed 77% to the overall measurement uncertainty.

3. 7. Advantages and Disadvantages

The main advantage of the method is that a large amount of sample (up to 150 g of soil and up to 100 g of plant material) can be processed, which is important in obtaining enough ^{129}I for determination and thus increasing the sensitivity and applicability of the method. This was mainly achieved by improving the ratio of KOH to sample during fusion. A second is that the separation of iodine following neutron irradiation is rapid (25 minutes) in comparison to literature methods (some hours).[3,4] Thirdly, previous methods were not verified by the use of reference materials. Finally, we showed that simple purification of the charcoal used in the pre-separation contributed appreciably to improving the limit of detection of the method.

The mean disadvantage of the method is the amount of chemicals that are needed to separate iodine (up to 300 g of pelletized KOH and 300 mL of $CHCl_3$ for one determination).

3. 8. Applicability

Dried samples of brown algae *Fucus virsoides* (100 g) from the Adriatic Sea were analysed by the method described and the results for ^{129}I are summarised in Table 6.

Hou et al.[3] investigated the content of ^{129}I in the brown algae *Fucus vesicolosus* collected in Denmark (Klint) and Iceland. Results obtained by them are shown in Table 6 and with the exception of Denmark (Klint), they are comparable to our values. This indicates the influence of ^{129}I discharged from Sellafield and La Hague, carried by ocean currents,[5] and in the case of the Adriatic Sea, by the atmospheric pathway.

4. Conclusions

To pre-concentrate iodine alkaline fusion in KOH and trapping/adsorption of iodine on activated charcoal was optimised. The advantages of the developed method are as follows: more than 150 g of sample can be used for the pre-concentration and after irradiation of the activated charcoal the duration of radiochemical procedure for separated induced radionuclide ^{130}I is about 25 minutes. In addition, the whole procedure was not time consuming in comparison with literature methods.[3,4] The destruction of the reference material IAEA 375 Soil by alkaline fusion yielded a chemical recovery for iodine of 60–70% and for marine algae 75–85%.

To minimise interfering nuclear reactions the charcoal used was cleaned to reduce the content of uranium. Treating the charcoal with aqua regia reduced the concentration of U to 0.54 mg kg^{-1} (by 64%), HCl (1 mol L^{-1}) to 0.69 mg kg^{-1} (by 54%) and HNO_3 (10 mol L^{-1}) to 0.60 mg kg^{-1} (by 60%).

Appropriate irradiation conditions were investigated and irradiation in the F ring was preferred, because the ratio between thermal and fast neutrons was 1 : 0.3, so the (n,γ) nuclear reaction with thermal neutrons predominates over (n,2n) nuclear reaction with fast neutrons, in contrast to the central channel where the ratio of thermal and fast neutrons is 1 : 1. Using the F ring of the TRIGA reactor we demonstrated that a ^{129}I/^{127}I ratio of 10^{-11} can be reached by RNAA.

The method developed for pre-separation of iodine by alkaline fusion and trapping on activated charcoal was found suitable for determination of ^{129}I in ultra trace levels. The method was validated using the reference material IAEA-375 Soil and good agreement was found between the obtained and recommended value.

Measurement uncertainty was evaluated for the method developed and the main uncertainty sources were

Table 6: Concentrations of ^{129}I and ^{127}I in brown algae *(Fucus virsoides)* and brown algae *(Fucus vesicolosus)*

Reference	**^{129}I (10^{-7} µg g^{-1})**	**^{129}I (10^{-3} Bq kg^{-1})**	**^{127}I (n = 4) (µg g^{-1})**	**^{129}I/^{127}I (10^{-12})**	**Ref.**
Slovene coast					
Ankaran	4.00 ± 1.04	2.65 ± 0.69	448.0 ± 34.1	~895	This work
Debeli rtič	4.34 ± 1.22	2.88 ± 0.81	505.9 ± 35.4	~860	
Rujkjavik Havn	12.50 ± 0.10	8.30 ± 0.07	277.0 ± 0.7	~4500	Hou et al.3
Iceland (1)	1.30 ± 0.08	0.86 ± 0.05	330.0 ± 0.7	~395	
Iceland (2)	2.16 ± 0.09	1.44 ± 0.06	364.0 ± 1.5	~597	
Denmark (Klint)	243.0 ± 2.2	161.4 ± 1.5	375.0 ± 5.3	~64800	
Denmark (Klint)	131 ± 1.0	87.0 ± 0.7	328.0 ± 4.2	~39900	

Results are given with measurement uncertainty (95% Confidence interval, k = 2) due to the repeatability of the chemical yield determination, the count rate of the induced nuclide in the $^{129}I/^{127}I$ working standard solution, the count rate of the induced nuclide in the sample and the certified uncertainty of the ^{129}I solution activity (Cerca Lea).

The method was applied to determine the content of ^{129}I in the marine algae *Fucus virsoides* collected along the Slovene coast and the results found were in the order of 4×10^{-7} µg g^{-1}.

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Povzetek

Razvili in optimizirali smo RNAA metodo za določitev ^{129}I v vzorcih iz okolja. Vzorec zemlje ali rastlinskega materiala (150 g) smo razgradili v alkalni talini, nato raztopili z vročo destilirano vodo, dodali Na_2SO_3 (10 %) ter raztopino nevtralizirali z H_2SO_4 (96 %). Jod smo oksidirali z $NaNO_2$ (10 %) in H_2SO_4 (2,5 mol L^{-1}), ga ekstrahirali v kloroform ter reducirali z Na_2SO_3 (10 %) v vodno fazo. Z $NaNO_2$ smo ga oksidirali ter v toku dušika adsorbirali na aktivno oglje. Optimizirali smo razmerje med maso vzorca in KOH, pretok dušika, čas izpihovanja, količino aktivnega oglja potrebnega za učinkovito adsorpcijo joda ter izboljšali čistočo oglja. Kemijska sestava oglja (sledovi K, Na, Br) vpliva na velikost doze akumulirane med obsevanjem ter podaljšuje čas hlajenja preden lahko izvedemo radiokemijsko separacijo radioizotopa ^{130}I induciranega z jedrsko reakcijo $^{129}I(n,\gamma)^{130}I$ ($t_{½}$ = 12,36 h, E_γ = 536 keV). Kemijski izkoristek celotnega postopka smo določili spektrofotometrično in preko jedrske reakcije $^{127}I(n,2n)^{128}I$. Meja detekcije metode za ^{129}I je 5×10^{-14} g g^{-1}.Ovrednotili smo tudi merilno negotovost postopka. Metodo smo uporabili za določitev vsebnosti ^{129}I v rjavi morski algi Jadranski bračič (*Fucus virsoides*), katero smo vzorčili vzdolž Slovenske obale. Rezultati za ^{129}I so bili reda velikosti 4×10^{-7} µg g^{-1}.