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^{129}I determination by direct gamma-X spectrometry and its application to concentration variations in two seaweed species

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Abstract. The quantification of radionuclides by direct gamma-X spectrometry with energy below 100 keV requires knowledge the elementary composition of the sample or the development of a device for determining the mass attenuation coefficients. This is especially true for ^{129}I which is characterised by a 29.8 keV X-ray and 39.6 keV gamma ray. Experimental equipment has been developed in order to obtain this mass attenuation coefficient as a function of energy. ^{129}I concentrations were measured in samples of seaweed (*Fucus serratus* and *Laminaria digitata*) collected monthly over a period of one year nearby La Hague reprocessing plant in France. This paper describes the measurement methodology used to determine ^{129}I concentrations and variations in the two seaweeds over a one-year period. Mean mass attenuation coefficients for ^{129}I energies were established in order to determine the self-attenuation corrective factor for both seaweed species, regardless of the sampling date.

1. INTRODUCTION

Iodine-129 is a beta emitter ($T_{1/2}$ = 1.57 × 10^7years) with both natural and artificially produced radionuclides existing in the environment. This radionuclide will decay to emit photons of energies below 40 keV at high intensity. Direct gamma-X spectrometry is therefore well suited to quantifying this radionuclide, provided that self-attenuation corrections are applied. These corrections must not only take into account the density but also the elementary composition of the matrix seeing that the photoelectrical process becomes the dominating interaction phenomenon under 100 keV. We recently developed a corrective method based on transmission measurements [1-2] to determine these self-attenuation correction factors in relation to standard calibration sources. Temporal variations in the self-attenuation coefficient are related to variations in the elementary composition of the matrix, including variations in iodine in the case of seaweed. Our study focused on brown seaweed, more specifically *Fucus serratus* and *Laminaria digitata*, which are used as bio-indicators in environmental studies to monitor various pollutants [3-9]. The specificity of such seaweed resides in their sedentary nature on the one hand and the fact that they concentrate elements that are only soluble in their surrounding environment on the other hand.

2. SAMPLING AND PREPARATION

Two sites located on each side of Cogema's waste reprocessing plant at La Hague in France were chosen for taking samples: Diélette (15 km from the release outlet) and Goury (5 km from the release outlet). Samples were taken from November 2002 to December 2003. Monthly samples of *Fucus serratus* – species found in the mediolittoral zone – were taken without interruption, whereas *Laminaria digitata* samples – developing in infralittoral zone – could only be taken during periods of great coefficients of tide.

After collection, samples were dried at 90°C to constant weight, before being ground and conditioned in 380 ml and 60 ml cylindrical containers. These containers were used respectively to determine the activity of radionuclides and the mass attenuation coefficients by means of gamma spectrometry.

3. MEASUREMENT METHODS

3.1 Quantification of ^{129}I by gamma spectrometry

Each sample was subjected to two measurements:

- standard gamma spectrometry to quantify radionuclides in samples using N-type HPGe detectors with a relative efficiency above 50% [10], and
- transmission in relation to the energy of a parallel flux of photons (collimator) with a planar detector in view of determining mass attenuation coefficients [1-2].

The gamma spectrometers were calibrated using Analytics or Cerca multi-elementary sources (water equivalent resin matrix, density = 1.15 g.cm^{-3}). The detection efficiency in relation to the photon energy was calculated in line with corrections regarding the true coincidences summing [11].

3.2 Quantification of total iodine by ionic chromatography

Each sample was subjected to two ionic chromatography measurements (Dionex DX 500) with an aliquot of approximately 25 mg. Iodine was separated by burning the sample in a Schöniger flask in the presence of a hydrazine hydrate and oxygen solution. The concentration of iodine (^{total}I) in the hydrazine hydrate solution was obtained by amperometric detection.

4. RESULTS – DISCUSSION

4.1 ^{total}I concentrations and specific activities of ^{129}I and ^{40}K

Figure 1 illustrates both the ^{total}I concentrations and the specific activities of ^{129}I and ^{40}K for *Fucus serratus* and *Laminaria digitata* samples taken between November 2002 and December 2003. Self-attenuation correction factors were integrated into these values. Only density correction factors for ^{40}K were used, to which a matrix correction factor was added in the case of ^{129}I [1]. Density corrections are generally applied in gamma metrology laboratories, which is not the case for matrix corrections as the elementary composition of a sample taken from the environment can vary greatly, even when the same species is used. Correction factors were determined based on the experimental value of the mass attenuation coefficient for measurements whose results are illustrated in figure 1 (cf. paragraph 4.2).

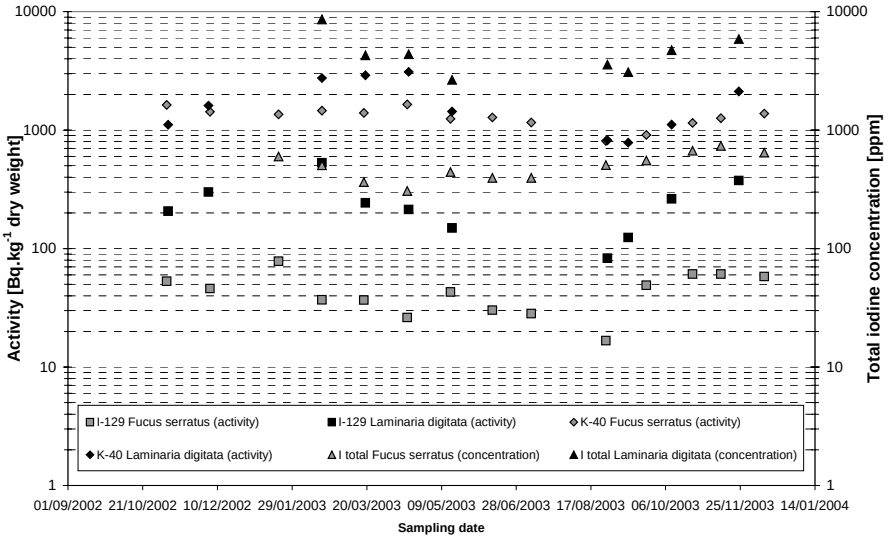
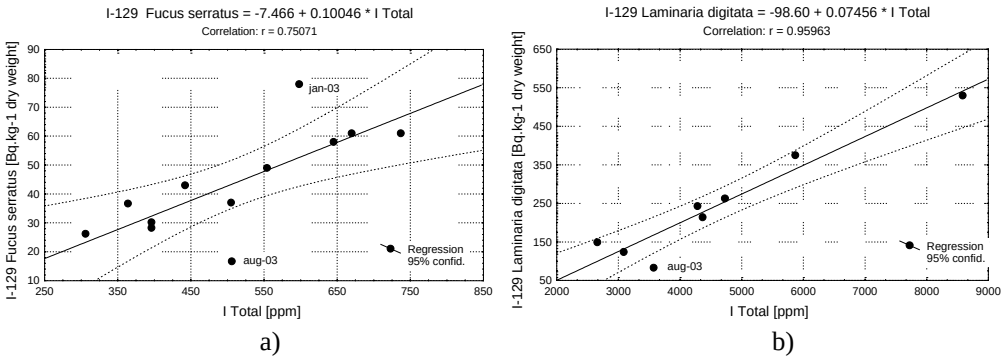


Figure 1. ^{total}I concentrations and specific activities of ^{129}I and ^{40}K in *Fucus serratus* and *Laminaria digitata* samples from November 2002 to December 2003.

For *Fucus serratus* and *Laminaria digitata* respectively, ^{129}I activities varied between (16.7 ± 2.5) and (78 ± 9) Bq.kg^{-1} dry weight and between (83 ± 8) and (530 ± 65) Bq.kg^{-1} dry weight, whereas ^{40}K varied between (810 ± 115) and (1645 ± 285) Bq.kg^{-1} dry weight and between (785 ± 110) and (3105 ± 665) Bq.kg^{-1} dry weight.

In terms of ^{total}I concentrations, results varied between (310 ± 60) and (740 ± 130) ppm and between (2660 ± 570) and (8580 ± 920) ppm for *Fucus serratus* and *Laminaria digitata* respectively. Concentrations measured in *Laminaria digitata* samples were systematically higher than those obtained in *Fucus serratus* samples due to the existence of an enzymatic system more specifically related to the accumulation of iodine in the *Laminaria digitata* species [12, 13].

Total iodine concentrations and ^{129}I activities correlated well during the observed period (figure 2), except for samples taken in August 2003 for both seaweed species and for *Fucus serratus* samples taken in January 2003. Statistical analysis (results not presented here) showed in-phase variations of ^{total}I and ^{129}I for both seaweed species. ^{total}I results determined by X-ray fluorescence for *Fucus serratus* samples from the Herquemoulin and Wimereux sites as reported by Patti [14] were consistent with results reached in our study: ^{total}I concentrations are not affected by the sample site and date. Furthermore, statistical analysis of such data (results not presented here) revealed a temporal variation in in-phase ^{total}I concentrations between the three sites (Diélette (this study), Herquemoulin and Wimereux [14]).



a) b)

Figure 2. Correlation between total iodine and iodine-129 for *Fucus serratus* (a) and *Laminaria digitata* (b).

Table 1 shows the $^{129}I/^{total}I$ isotope ratios for samples taken in 2003. It appears that the yearly variation in this ratio could be due to both the variation in ^{129}I releases and the biological cycle of these bio-indicators.

The $^{129}I/^{total}I$ isotope ratio in the ocean, in the absence of any anthropogenic contribution, is estimated at 10^{-12}, whereas this value approaches 2×10^{-11} at the end of the nuclear arms testing period [15]. Values obtained in the English Channel are much higher owing to industrial nuclear releases. In 1982, Patti [14] calculated a $^{129}I/^{total}I$ isotope ratio of 4.3×10^{-7} for a *Fucus serratus* sample taken in Diélette.

At the same site, between November 2002 and December 2003, we calculated a $^{129}I/^{total}I$ isotope ratio between 0.5×10^{-5} and 2×10^{-5} (table 1) for *Fucus serratus* and a ratio between 3.5×10^{-6} and 9.6×10^{-6} for *Laminaria digitata* (table 1).

$^{129}I/^{total}I$ isotope ratios calculated for the *Fucus serratus* species are superior to those calculated for the *Laminaria digitata* species, whereas ^{129}I and $^{total}I$ concentrations are greater in the *Laminaria digitata* species. This could be due to the different locations of the sampling sites in relation to the reprocessing plant outlet. The same observation was made in 1997 [16] for samples of the same seaweed species carried out at different sites located near the release outlet, whereas at greater distances from the release outlet, the isotope ratios obtained for both species were identical. Two hypotheses could explain why the *Fucus serratus* species has a higher isotope ratio than the *Laminaria digitata* species:

- differing iodine metabolisms and/ or incorporation kinetics of the two species,
- a different yearly immersion period for *Fucus serratus* and *Laminaria digitata* (the two species do not develop at the same depth).

Table 1. $^{129}I/^{total}I$ isotope ratios for *Fucus serratus* and *Laminaria digitata* samples.

Sampling date	Specie	$^{129}I/^{total}I$	Sampling date	Specie	$^{129}I/^{total}I$
20/01/2003	*Fucus serratus*	1.96E-05 ± 2.5E-06	18/02/2003	*Laminaria digitata*	9.28E-06 ± 9.3E-07
18/02/2003	*Fucus serratus*	1.10E-05 ± 1.6E-06	19/03/2003	*Laminaria digitata*	8.5E-06 ± 1.4E-06
18/03/2003	*Fucus serratus*	1.52E-05 ± 2.1E-06	17/04/2003	*Laminaria digitata*	7.4E-06 ± 1.2E-06
16/04/2003	*Fucus serratus*	1.29E-05 ± 2.1E-06	16/05/2003	*Laminaria digitata*	8.4E-06 ± 1.7E-06
15/05/2003	*Fucus serratus*	1.46E-05 ± 2.2E-06	28/08/2003	*Laminaria digitata*	3.49E-06 ± 5.8E-07
12/06/2003	*Fucus serratus*	1.15E-05 ± 1.7E-06	11/09/2003	*Laminaria digitata*	6.0E-06 ± 1.0E-06
08/07/2003	*Fucus serratus*	1.07E-05 ± 1.7E-06	10/10/2003	*Laminaria digitata*	8.4E-06 ± 1.3E-06
27/08/2003	*Fucus serratus*	4.96E-06 ± 8.2E-07	24/11/2003	*Laminaria digitata*	9.6E-06 ± 1.6E-06
23/09/2003	*Fucus serratus*	1.33E-05 ± 2.3E-06			
24/10/2003	*Fucus serratus*	1.37E-05 ± 2.1E-06			
12/11/2003	*Fucus serratus*	1.24E-05 ± 2.0E-06			
11/12/2003	*Fucus serratus*	1.35E-05 ± 2.1E-06			

4.2 Mass attenuation coefficients for gamma-X rays of ^{129}I

An attenuation correction factor at low energy was calculated using the mass attenuation coefficient of each seaweed species [1-2]. The coefficients for gamma-X rays of ^{129}I for *Fucus serratus* and *Laminaria digitata* are represented in table 2 and 3 respectively. Values vary to a lesser extent – 4% to 6% of the standard deviation within 1 sigma – for *Fucus serratus* (table 2) than for *Laminaria digitata* where a variation of approximately 20% was obtained. This rather marked dispersion is due to the great variation in the different elements, including $^{total}I$, during the entire period (figure 1).

For energies above 100 keV, self-attenuation corrections in gamma-ray spectrometry result from the difference in sample densities in relation to the density of the calibration source. Below 100 keV where the photoelectrical effect increases considerably, the elementary composition of the matrix becomes the main corrective factor. The relative importance of these two parameters for gamma-X rays of ^{129}I is illustrated by the results in table 4, which lists the activities after density corrections only, and then with additional corrections due to the matrix's composition. While density corrections remain below 10% for these measurements, matrix corrections can exceed 100%. Corrections are greater in the case of the *Laminaria digitata* species – even though the container (35 mm) used in this case was thinner than that used for the *Fucus serratus* species (59 mm) – due to the greater concentration of elements, including iodine, in this species.

Table 4. Activities of ^{129}I calculated using different gamma-X rays measured for two samples for this study in relation to the applied correction factors.

	Fucus aug-03 N°LMRE 34022		*Laminaria* mar-03 N°LMRE 31659	
Container	(V=380 ml, H=59 mm)		(V=220 ml, H=35 mm)	
Weight (g)	365.6		235.1	
Density (g.cm^{-3})	0.96		1.07	
E [keV]	Activities after density corrections only	Activities after density corrections and with additional corrections due to the matrix's composition	Activities after density corrections only	Activities after density corrections and with additional corrections due to the matrix's composition
29.5 (X-ray)	8.8 ± 2.1	17 ± 4	90 ± 11	218 ± 27
29.8 (X-ray)	8.6 ± 1.3	16.7 ± 2.5	101 ± 11	243 ± 27
39.6 (γ-ray)	11.0 ± 1.4	16.5 ± 2.1	129 ± 15	237 ± 28

5. CONCLUSION

Contrary to other radionuclides released into the environment by the nuclear industry, very little data on ^{129}I has been produced by radioecological monitoring programmes and studies owing to the difficulty of measuring this radionuclide. The quantification of this isotope using direct gamma-X spectrometry requires considerable self-attenuation corrections, often greater than 100%.

In terms of the two seaweed species, *Fucus serratus* and *Laminaria digitata*, that are often used as marine bio-indicators of both radioactive and non-radioactive pollution, we calculated the mean mass attenuation coefficients for dry samples to correct the detection efficiencies of the self-attenuation phenomenon of ^{129}I. This study was performed over a yearly period so as to integrate temporal variations in the constituents of both seaweed species. The standard deviation of the average value of this coefficient is equivalent to about 5% for *Fucus serratus* and 20% for *Laminaria digitata*.

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Table 2. Mass attenuation coefficients for gamma-X rays of ^{129}I for *Fucus serratus*.

mass attenuation coefficient [$cm^2.g^{-1}$] *Fucus serratus* (dry)														
N°LMRE	*30210*	*30211*	*31197*	*30897*	*33045*	*31998*	*32317*	*33265*	*33268*	*34022*	*34002*	*34315*	*40044*	*40165*
Sampling date	nov-02	déc-02	janv-03	févr-03	mars-03	avr-03	mai-03	juin-03	juil-03	aou-03	sept-03	oct-03	nov-03	déc-03
E (keV)														
29.5	0.774	0.789	0.770	0.719	0.729	0.717	0.704	0.721	0.661	0.639	0.669	0.751	0.726	0.727
29.8	0.759	0.775	0.756	0.706	0.718	0.704	0.691	0.711	0.652	0.630	0.659	0.741	0.716	0.717
39.6	0.461	0.466	0.457	0.426	0.440	0.426	0.421	0.437	0.410	0.403	0.422	0.460	0.444	0.444

mass attenuation coefficient [$cm^2.g^{-1}$] *Fucus serratus* (dry)					
E (keV)	mean	standard deviation	min	max	dispersion %
29.5	0.721	0.043	0.639	0.789	6
29.8	0.710	0.042	0.630	0.775	6
39.6	0.437	0.020	0.403	0.466	4

Table 3. Mass attenuation coefficients for gamma-X rays of ^{129}I for *Laminaria digitata*.

mass attenuation coefficient [$cm^2.g^{-1}$] *Laminaria digitata* (dry)													
N°LMRE	*30459*	*30607*		*31122*	*31659*	*32003*	*32319*			*34024*	*34012*	*34317*	*40046*
Sampling date	nov-02	déc-02	janv-03	févr-03	mars-03	avr-03	mai-03	juin-03	juil-03	aou-03	sept-03	oct-03	nov-03
E (KeV)													
29.5	0.725	0.837		1.116	0.992	0.999	0.759			0.626	0.615	0.71	0.964
29.8	0.711	0.819		1.089	0.972	0.978	0.744			0.616	0.606	0.698	0.949
39.6	0.521	0.607		0.769	0.641	0.624	0.487			0.455	0.440	0.503	0.664

mass attenuation coefficient [$cm^2.g^{-1}$] *Laminaria digitata* (dry)					
E (keV)	mean	standard deviation	Min	max	dispersion %
29.5	0.834	0.174	0.615	1.116	21
29.8	0.818	0.169	0.606	1.089	21
39.6	0.571	0.106	0.440	0.769	19