^{129}I and ^{129}I/^{127}I ratio measurements in environmental samples by RNAA, AMS and direct γ-X spectrometry. Intercomparison exercises

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Abstract. ^{129}I, is a natural long-lived isotope, with a half-life of 15.7 million years, also artificially produced in nuclear power plant and released in liquid and gaseous effluents of nuclear fuel reprocessing plants. Due to the lack of environmental international reference material for ^{129}I, interlaboratory comparison exercises are very rare and validation of new measurement techniques is very difficult to achieve. This study presents three intercomparison exercises on the ^{129}I and ^{129}I/^{127}I measurements using three different techniques : Radiochemical Neutron Activation Analysis, Accelerator Mass Spectrometry and direct γ-X spectrometry associated with Ionic Chromatography. The first intercomparison was performed on a *Fucus serratus* sample, leading to propose it as a reference material. The others intercomparison exercises were performed on samples of different biological matrices, marine and terrestrial, presenting various ^{129}I activity levels. The different intercomparison exercises results showed a good agreement between the three techniques on the considered environmental matrices, for samples with ^{129}I activity comprised between 0.2 and 200 Bq.kg^{-1} dry weight.

1 INTRODUCTION

Iodine-129 is a natural radionuclide also artificially produced by civil and military activities. Due to its long half-life (15.7×10^6 years), its activity levels have increased with time in the environment. Pre-nuclear age ^{129}I/^{127}I ratio was comprised between 10^{-12} and 10^{-9}, today it reaches levels of about 10^{-6} in the vicinity of nuclear fuel reprocessing plants [1, 2]. ^{129}I appeared to be one of the major radionuclide to contribute to the dose to population when assessing the impact of the radioactive effluent discharges from nuclear spent fuel reprocessing plant [3]. The monitoring of environmental indicators shows a large activity range that can be measured by three techniques.

Radiochemical Neutron Activation Analysis (RNAA) has been used since the fifties for the measurement of ^{129}I/^{127}I ratios [4, 5] and in the eighties appeared the use of Accelerator Mass Spectrometry (AMS) [6, 7]. ^{129}I measurement by direct γ-X spectrometry with self-absorption correction was developed in the last few years [8]. While RNAA and AMS need a specific sample preparation, including dissolution of the sample and radiochemical processing, that can be a source of major result differences [9, 10], direct γ-X spectrometry allows to measure homogeneous ground dried samples.

The lack of environmental certified reference material for ^{129}I compels measurement laboratories to make their own internal reference material used in quality assurance control. The chronic discharges of ^{129}I in authorized low-level radioactive liquid and gaseous effluents of the La Hague nuclear reprocessing plant reach an estimated amount of 1305 kg [3]. Thus, the various natural components of the La Hague environment are contaminated at different levels and can be used to process reference materials characteristic of bioindicators used in classical radioactivity monitoring of nuclear plants.

2 MATERIALS AND METHODS

2.1 Strategy of sampling

The strategy of sampling was defined to allow the comparison of the three measurement techniques using different natural materials. Firstly, the elaboration of a reference material with an ^{129}I activity level higher than the highest detection limit of the three measurement techniques and in sufficient quantity to allow to carry out a type B intercomparison test. Then, a set of samples of the same species presenting an ^{129}I activity gradient, which makes it possible to compare the various methods on a range of activities

covering at least an order of magnitude. And finally, a set of samples of different environmental matrices with different ^{129}I levels in order to point out a possible matrix effects on the methods results.

These samples of different nature and different species were collected along the littoral of the North Cotentin and the French Channel coast (Figure 1), zone under the direct and long-distance influence of the discharges of authorized low-level radioactive effluents of the reprocessing plant of La Hague.
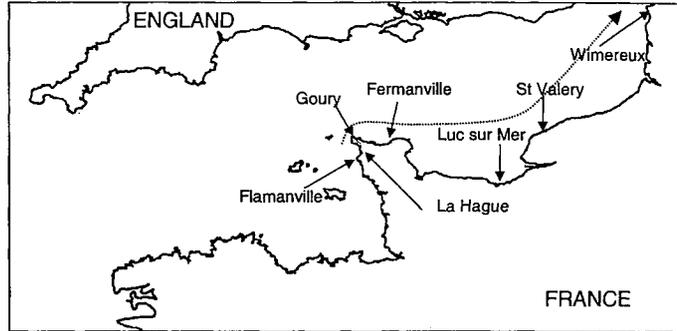

Figure 1 : Location of the sampling stations along the French Channel coast.
The dotted arrow indicates the direction of the main marine current.

2.1.1   Reference material FC98

Algae are regarded as sentinel bioindicators of marine environmental pollution. The brown algae most usually taken for the monitoring of the radioactivity of the Atlantic seaside is the *Fucus serratus* [3]. The reference material FC98 was thus made up starting from a sample of 100 kg fresh of *Fucus serratus* collected on January 12th 1998 on a homogeneous zone of the shore, at the entrance of the port of Goury.

2.1.2   Samples of the same species covering a range of activity

The same vegetal species appear on the same types of substrates of the Atlantic coast and it was shown that the artificial radionuclides contamination decreases when the distance of the sampling station at the outlet of La Hague increases [1]. Two types of samples, a brown algae, *Fucus serratus,* and a lichen, *Xanthoria parietina,* were collected simultaneously, on October 25th-28th, 1999, on 6 sites along the French Channel coast (Figure 1) to constitute two sets of samples presenting an ^{129}I activity gradient.

2.1.3   Samples of different species

The elementary composition of the environmental matrices is likely to interfere when measuring ^{129}I measurement. Samples of various marine and terrestrial plants like lichens, grass and fruits were collected on a transect line at the Goury coast.

2.2   Preparation of the samples and sub-sampling

All the samples were prepared for their measurement in line with AFNOR standards recommendations [11-14]. The material intended for type B intercomparison tests must "be subdivided into aliquot in a random way and its homogeneity must be guaranteed in order to ensure the representativity of the measurements carried out on each one of them" [15]. A particular attention was paid to the control of the drying temperature and to the granulometry of the final dried powder.

After the collection and a first cleaning on site, sample is then dried in a ventilated oven at a fixed temperature and controlled between 60 and 80°C. When a constant dried mass is reached, the sample is removed from the epiphytes organisms and coarsely ground in a knives Waring blender. It is then crushed more finely using an ultra-centrifugal blender from Retsch. This type of equipment, using a gauged sieve, allows defining the maximum size of the particles. In the case of large size samples, more than 1 kg of dried matter, after homogenisation, the division in sub-samples, is performed using an automatic distributor PT1000 from Retsch.

2.3 Measurements of iodine-129

2.3.1 Direct γ- X spectrometry with self-absorption correction.

The measurement of activity is performed using the X-emission line at 29.7 keV and the γ-emission peak at 39.5 keV. A second transmission measurement allows determining the self-absorption correction factor used to correct the measured activity. The measurement procedures, the installations used and their associated performances are described in other publications [8].

2.3.2 Methods of measurements with radiochemistry: RNAA and AMS

The first radiochemical stages (sample dissolution and selective extraction of iodine) are common whereas the final source precipitation stages are specific of each measurement technique (Figure 2). Detailed procedures are given in a previous report [16].
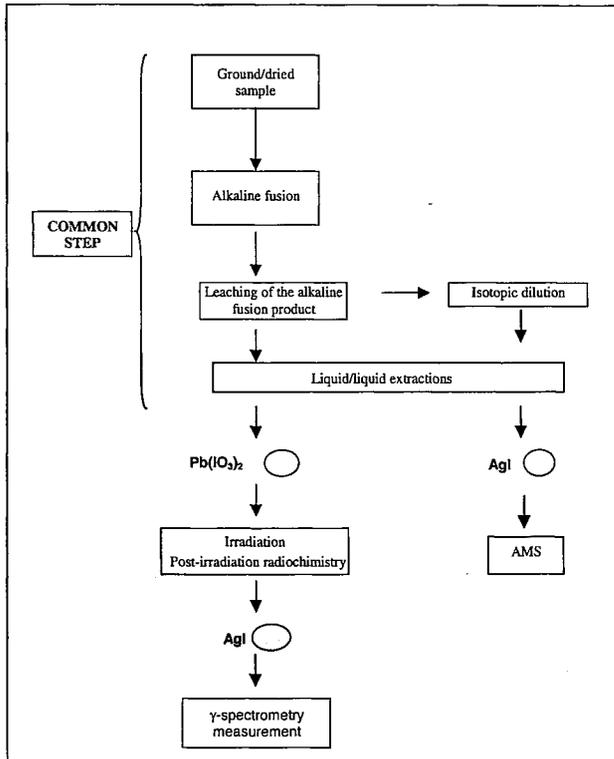

Figure 2 : Scheme of the radiochemical procedures used for the preparation
of the various sources needed for RNAA and AMS measurements.

3 RESULTS

3.1 Sample homogeneity

The multielementary composition of the FC98 reference material was characterized and its homogeneity checked [17] before to carry out the type B intercomparison test. Transmission results proved that it presents a satisfactory homogeneity down to a test mass of approximately 60 g. Analyses by Ionic Chromatography (IC) showed that its stable iodine concentration is homogeneous for masses down to 25 mg. The material FC98 was thus considered suitable as reference material in intercomparison tests. All the other samples collected for the various studies mentioned in this work were prepared in a similar way with homogeneity adequate for the intercomparison exercises.

3.2 Intercomparisons

3.2.1 Intercomparison 1 – Reference material FC98

FC98 was randomly aliquoted. Five aliquots were measured by direct γ- X spectrometry, six aliquots were prepared for RNAA and three others for AMS (Table 1).

Table 1 : ^{129}I and ^{129}I/^{127}I of reference material FC98 measured by direct γ- X spectrometry, AMS and RNAA associated with Ionic Chromatography. Stable iodine : 769 ± 46 ppm.

Results	^{129}I/^{127}I (10^{-5} g.g^{-1})				^{129}I (Bq.kg^{-1} d.w.)			
Technique of measurement	RNAA	AMS/IC	γ/IC 29.7keV	γ/IC 39.5keV	RNAA/IC	AMS/IC	γ 29.7keV	γ 39.5keV
	1.22 ± 0.12	1.37 ± 0.19	1.36 ± 0.11	1.39 ± 0.14	61.3 ± 7.1	68.7 ± 10.5	68.3 ± 4.1	69.9 ± 5.9
	1.06 ± 0.11	1.42 ± 0.20	1.42 ± 0.17	1.35 ± 0.17	53.3 ± 6.2	71.3 ± 10.9	71.3 ± 7.4	67.6 ± 7.7
	1.28 ± 0.13	1.46 ± 0.20	1.39 ± 0.16	1.35 ± 0.15	64.3 ± 7.5	73.5 ± 11.2	69.7 ± 6.7	67.7 ± 6.4
	1.36 ± 0.14		1.50 ± 0.21	1.43 ± 0.17	68.3 ± 8.0		75.2 ± 7.4	72.0 ± 7.4
	1.26 ± 0.13		1.71 ± 0.18	1.55 ± 0.18	63.3 ± 7.4		86.1 ± 7.7	78.1 ± 7.8
	1.14 ± 0.11				57.3 ± 6			
Mean	1.22	1.42	1.48	1.41	61.3	71.2	74.1	71.1
Median	1.24	1.42	1.42	1.39	62.3	71.3	71.3	69.9
2σ Standard Deviation (%)	17.47	6.37	19.08	11.73	17.4	6.8	19.4	12.2

The curve fitted on the frequency distribution computed for 5 classes shows a symmetrical Gaussian shape (Figure 3). The lowest values are obtained by RNAA whereas the results of AMS and direct γ- X spectrometry are distributed in a random way.

A research of the possible outliers was carried out by the calculation of z values. The two results corresponding to the extreme points of the data set can be considered as outliers.
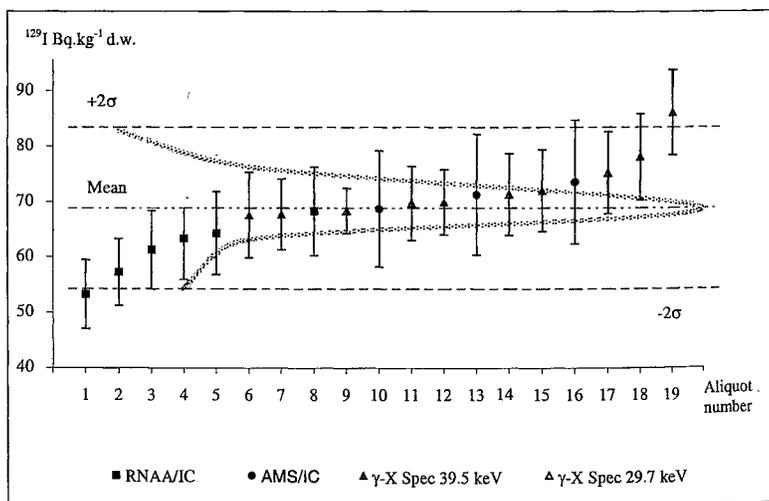

Figure 3 : Results obtained by the three methods of measurement ranked in ascendant order with superposition of the envelope of the distribution of the values.

The outlier values excluded, the estimated recommended average value is 68.7 Bq.kg^{-1} d.w. and equal to that of the median value, the 2σ standard deviation is 10.2 Bq.kg^{-1} d.w., corresponding to a relative standard deviation of 14.9%.

3.3 Intercomparison 2 - Samples of the same species covering a range of activity

One aliquot of each sample was analysed by the three methods of measurement (Table 2). The results on *Fucus serratus* obtained by the three methods present ^{129}I activities and ^{129}I/^{127}I ratios that vary over an order of magnitude. Lichens, collected on substrates under the influence of the sea spray, present activities much lower than those measured on algae.

Table 2 : Stable I , ^{129}I/^{127} and ^{129}I obtained by the three methods of measurement on the samples of *Fucus serratus* and *Xanthoria parietina* collected on six stations along the French Channel.

Site	Specie	Stable I mg.kg^{-1} d.w.	^{129}I/^{127}I (10^{-5} g.g^{-1})			^{129}I (Bq.kg^{-1} d.w.)		
			RNAA	AMS	γ/IC	RNAA/IC	AMS/IC	γ
Flamanville	*Fucus*	498.3 ± 29.9	1.10 ± 0.11	1.25 ± 0.18	1.23 ± 0.08	35.8 ± 4.2	41.0 ± 6.2	40.1 ± 1.1
	Xanthoria	30.8 ± 1.8	0.51 ± 0.05	0.69 ± 0.10	0.6 ± 0.3	1.02 ± 0.12	1.40 ± 0.21	1.2 ± 0.6
Goury	*Fucus*	882.0 ± 52.9	1.05 ± 0.11	1.16 ± 0.16	0.93 ± 0.09	60.5 ± 7.0	66.9 ± 10.2	53.8 ± 4.1
	Xanthoria	30.7 ± 1.8	1.26 ± 0.01	1.49 ± 0.21	0.90 ± 0.35	2.53 ± 0.30	2.99 ± 0.45	1.8 ± 0.7
Fermanville	*Fucus*	916.4 ± 55.0	0.47 ± 0.05	0.51 ± 0.07	0.56 ± 0.06	28.2 ± 3.3	30.7 ± 4.7	33.7 ± 2.8
	Xanthoria	19.9 ± 1.2	0.71 ± 0.07	0.80 ± 0.11	0.64 ± 0.32	0.92 ± 0.19	1.04 ± 0.16	0.8 ± 0.4
Luc sur Mer	*Fucus*	679.5 ± 40.8	0.26 ± 0.03	0.31 ± 0.04	0.28 ± 0.04	11.9 ± 1.4	14.1 ± 2.1	12.6 ± 1.6
	Xanthoria	29.4 ± 1.8	0.30 ± 0.03	0.41 ± 0.07	< 7.28	0.57 ± 0.07	0.79 ± 0.12	< 14
St Valery	*Fucus*	658.6 ± 39.5	0.29 ± 0.03	0.28 ± 0.04	0.28 ± 0.03	12.6 ± 1.5	12.4 ± 1.9	12.3 ± 1.1
	Xanthoria	4.7 ± 0.3	0.36 ± 0.07	0.60 ± 0.08	< 48.70	0.11 ± 0.02	0.18 ± 0.03	< 15
Wimereux	*Fucus*	529.0 ± 31.7	0.27 ± 0.03	0.40 ± 0.05	0.26 ± 0.04	9.3 ± 1.1	13.8 ± 2.1	9.3 ± 1.2
	Xanthoria	9.8 ± 0.6	0.26 ± 0.13	0.47 ± 0.07	2.5 ± 1.1	0.16 ± 0.08	0.30 ± 0.05	1.60 ± 0.7

The results obtained by the three measurement techniques show a positive correlation for the two matrices. The values obtained by RNAA/IC are more often the lowest, confirming the observation made on the results obtained on reference material FC98. The values obtained by the two other techniques are regularly distributed around the average values. However, a Student T-test, carried out on the results given by RNAA and AMS, does not highlight any significant difference between the two measurement techniques.

Only one result obtained by direct γ- X spectrometry on the Wimereux lichen sample is higher than those obtained by AMS and RNAA. This difference and the relative importance of uncertainties associated with γ- X spectrometry results are explained by the fact that the activities measured on the lichens are very close to the detection limit of this method.

The results on *Fucus serratus* and *Xanthoria parietina* samples show the same relative decreasing geographical gradient with the distance of the sampling stations from the outlet of the liquid effluents of the La Hague reprocessing plant.

3.4 Intercomparison 3 - Samples of different species

To confirm the conclusions drawn from the previous intercomparison results and to check that the methods of measurement lead to coherent results whatever the type of environmental matrix measured, a third intercomparison was conducted using RNAA and direct γ-X spectrometry. AMS was not used as the number of runs was limited and high levels of ^{129}I/^{127}I ratio in the samples collected along the French Channel don't require the use of this method.

The set of results (Table 3) doesn't highlight any systematic bias, in particular none of the techniques underestimates the average value systematically, as it was the case for the RNAA in the the two others intercomparisons. The Bravais-Pearson correlation coefficient reaches 0.999 and a T-test for paired results is highly significant and showed that there is no induced matrix effect.

Table 3 : Stable I , $^{129}I/^{127}$ and ^{129}I obtained by γ-X Spectrometry and RNAA on the samples from Goury.

Sample specie	Stable I mg kg^{-1} d.w.	$^{129}I/^{127}I(.10^{-6}$ g.g$^{-1})$ γ spec/IC	RNAA/IC	^{129}I Bq.kg^{-1} dry weight γ spec	RNAA/IC
Laminaria digitata (lamina)	5500 ± 330	5.43 ± 0.46	5.45 ± 0.54	195 ± 12	195.9 ± 22.8
Laminaria digitata (roots)	3152 ± 189	5.61 ± 0.52	5.88 ± 0.59	115.5 ± 8.2	121.1 ± 14.1
Palmaria palmata	87.4 ± 5.2	11.0 ± 1.8	10.6 ± 1.2	6.3 ± 1.0	6.0 ± 0.8
Ulva lactuca	88 ± 5.2	10.3 ± 2.0	10.3 ± 1.2	5.9 ± 1.1	5.9 ± 0.8
Fucus serratus	912.5 ± 54.7	9.82 ± 0.77	9.24 ± 0.92	58.5 ± 2.9	55.1 ± 6.4
Ramalina siliquosa	18.7 ± 1.1	8.29 ± 1.33	7.67 ± 0.89	1.01 ± 0.15	0.9 ± 0.1
Grass	42.1 ± 2.5	3.89 ± 1.00	4.4 ± 0.51	1.07 ± 0.27	1.2 ± 0.2
Excrement of cow	20.6 ± 1.2	2.0 ± 0.6	2.68 ± 0.31	0.27 ± 0.08	0.36 ± 0.05
Rubus sp.	4.4 ± 0.3	16.5 ± 7.8	13.0 ± 1.5^{-5}	0.47 ± 0.22	0.37 ± 0.05

4　CONCLUSION

The three intercomparison tests run between RNAA, AMS and direct spectrometry γ-X show the coherence of the results obtained by the three measurement techniques on environmental samples of different natures. The agreement covers specific activities measured between 0.2 Bq.kg^{-1} dry weight for the excrement of cow to 195 Bq.kg^{-1} dry weight for the blades of the algae *Laminaria digitata*.

They also made it possible to measure the relative importance of the environmental impact of the liquid discharges of ^{129}I of the reprocessing centre of La Hague using direct γ- X spectrometry on the relevant bioindicator samples. This last method is the easiest measurement technique currently used in surveillance laboratory in charge of the routine monitoring of the ^{129}I contamination of the environment.

Aknowledgements

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