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# Microwave-based digestion method for extraction of $^{127}$I and $^{129}$I from solid material for measurements by AMS and ICP-MS

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ABSTRACT

This work presents a microwave-based digestion method followed by a radiochemical extraction procedure to extract iodine from environmental matrices that provides iodine in a form suitable for the measurement of $^{129}$I by AMS, with shorter preparation times, small sample sizes and higher automation than previous methods. Samples were digested by a microwave digestion method in closed vessels using $HNO_3$ as oxidizing agent. Following chemical iodine extraction consisted in an organic compound extraction followed by an aqueous solution extraction and iodine precipitation. Prepared samples were used to measure $^{127}$I by ICP-MS and $^{129}$I by AMS. The method was validated by ICP-MS measuring $^{127}$I content in standard reference materials covering a wide variety of biological, soil and sediment matrices: 1547 Peach Leaves, 1537a Tomato Leaves, 1549 Non-Fat Milk Powder, 2704 Buffalo River Sediment, 2711 Montana Soil and 1648 Urban Particulate Matter from the National Institute of Standards and Technology, IAEA-375 Soil and IAEA SL-1 Lake Sediment from the International Atomic Energy Agency and 186 Pig Kidney from Community Bureau of Reference. The recoveries with respect to the reference values were about 90%. Iodine losses during chemical extraction could be due to its volatilization as HI or I2 in acid means. Accurate results for determination in certified materials and good recoveries.

## 1. Introduction

Iodine is an essential micronutrient for animals and human, mainly because it is a constituent of the thyroid hormones. Excessive or deficient iodine intake results in a variety of human thyroid dysfunction and disorder, as hyperthyroidism. The determination of iodine in biological, clinical and environmental samples has received considerable attention during the last few decades as it is considered as essential trace element which plays an important role in human metabolic processes [1]. Whilst $^{127}$I is the only stable isotope, the most hazardous iodine species are the radioactive isotopes such as $^{129}$I and $^{131}$I. $^{129}$I accumulates in the environment as a result of nuclear weapon testing, nuclear accidents and emissions from nuclear fuel reprocessing plants because of its long half life ($15.7 \times 10^6$ years) [2] and can enter the food chain via the air as a result of these aerial emissions. Its potential effect on humans is considerable since iodine and its compounds are volatile and highly mobile in the environment, easily entering humans via ingestion or inhalation.

The present knowledge about the radioecology of $^{129}$I is strongly biased by the analytical capabilities of radiochemical neutron activation analysis (RNAA). Since 1962, when RNAA was used the first time for $^{129}$I analysis in biological materials [3], this method remained the only method applicable to environmental $^{129}$I analysis for many years. Typical samples suitable for RNAA include materials with a high content of $^{127}$I (thyroids, seaweed and algae) and isotopic $^{129}$I/$^{127}$I ratios higher than $10^{-10}$, samples with low content of $^{127}$I (soils) and isotopic ratios higher than $10^{-9}$, and samples with a very low content of $^{127}$I (plants) and isotopic ratios higher than $10^{-8}$ [4]. Since 1980, accelerator mass spectrometry (AMS) which had already been applied to the investigation of other long-lived isotopes is used for analysis of $^{129}$I [5–7]. All “low-level” samples, which have $^{129}$I/$^{127}$I ratios below $10^{-9}$ and therefore are difficult or impossible to analyze by RNAA, can be analyzed precisely by AMS. By AMS the $^{129}$I/$^{127}$I isotopic composition of the sample material is measured. To obtain absolute $^{129}$I concentrations, information on the total $^{127}$I content of the sample material is needed, which can be determined by several techniques.

In order to determine low concentration levels of $^{127}$I ($\mu g\, g^{-1}$ and $ng\, g^{-1}$ levels), sensitive analytical methods are required. A variety of analytical methods have been used for its determination in several kind of samples, including spectrophotometry [8], ion selective electrode [9,10], X-ray fluorescence analysis [11], ion chromatography [12,4] (IC), gas chromatography mass spectrome-

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try [13,14], voltammetry (mainly cathodic stripping voltammetry) [15,16], inductively coupled plasma optical emission spectrometry (ICP-OES) [17,18] and inductively coupled plasma mass spectrometry (ICP-MS) [1,19–21]. For the determination step ICP-MS is a very good technique since it provides excellent detection power, high sensitivity and sample throughput for $^{127}$I determinations [19,21].

However, despite some analytical techniques allowing $^{127}$I and $^{129}$I determination with low limits of detection, as, e.g., ICP-MS and AMS, the main problem is still the sample decomposition and separation step. Because of its physical and chemical properties, iodine can be lost partially or totally by volatilization and/or transformation into a chemical form not suitable for the particular measurement [22]. For the measurement of $^{129}$I, extraction of iodine from solid materials has been carried out by combustion (in conjunction with RNAA and AMS analysis) and leaching methods (in conjunction with AMS analysis). Although these methods have proved to be reliable and have a high extraction yield their main disadvantages would be the long time needed for the total leaching or combustion and, in some cases, the use of relatively large amount of sample. Studier et al., [3] applied a combustion method that needed large amount (up to 100 g) of solid material and 3 h to get complete sample combustion in conjunction with the Neutron Activation Analysis for measurement of $^{129}$I. Englund et al. [23] shows another combustion method in conjunction with AMS analysis of $^{129}$I which needed up to 1.5 g of sample material and between 2 and 3 h to get the complete sample combustion. Oktay et al., [24] applies an alkaline leaching method which needed 20 g of sample and 6 h to get complete sample leaching. However, use of relatively large amount of sample combined with the difficulties in the determinations of $^{129}$I in environmental samples [25,26] encouraged us to explore possibilities for an alternative microwave digestion based procedure with smaller sample sizes.

The purpose of this study was to develop a microwave-based digestion method followed by a radiochemical extraction procedure to extract iodine from environmental matrices that would provide iodine in a form suitable for the measurement of $^{129}$I by AMS, looking for shorter preparation times, small sample sizes and higher automation. The whole separation procedure was validated to detect iodine chemical losses measuring $^{127}$I concentrations by ICP-MS in several reference materials. Further validation of the method is provided by measuring by AMS three certified reference materials with known concentrations of $^{129}$I isotope.

## 2. Iodine separation

In the method presented here, samples were digested in closed vessels at 200 °C in a microwave using $HNO_3$ as oxidizing agent and following chemical iodine extraction, which consisted in an organic compound extraction followed by an aqueous solution extraction and iodine precipitation. After the whole procedure was completed, aliquots of the solutions were used to measure $^{127}$I using ICP-MS. For the determination of $^{129}$I by AMS samples were prepared by addition of 2 mg of iodine carrier before microwave-based digestion. Measurements of $^{127}$I content in samples were performed at the ICP-MS Unit of the Servicio de Investigación Agraria (University of Seville, Spain) meanwhile $^{129}$I measurements were performed at Accelerator Mass Spectrometry Unit of the Centro Nacional de Aceleradores (CNA, University of Seville, Spain).

The method was tested by ICP-MS using the standard reference materials (SRMs) 1547 Peach Leaves, 1537a Tomato Leaves, 1549 Non-Fat Milk Powder, 2704 Buffalo River Sediment, 2711 Montana Soil and 1648 Urban Particulate Matter from National Institute of Standards and Technology (NIST). Also IAEA-375 Soil sample and IAEA SL-1 Lake Sediment from the International Atomic Energy Agency and BCR 186 Pig Kidney from Community Bureau of Reference were used in this study. These standards have certified or reference values for the concentration of $^{127}$I. For AMS measurements three standard materials from IAEA with certified or reference values for $^{129}$I concentration were used: soil (IAEA-375), mixed fish from the Irish Sea and North Sea (IAEA-414) and Mediterranean mussel (IAEA-437).

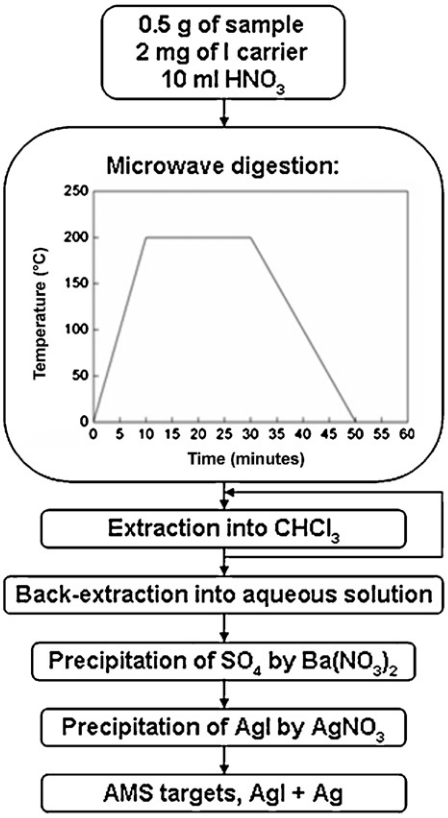

**Fig. 1.** Flow chart summarizing the iodine extraction procedure.

### 2.1. Microwave digestion procedure

All samples were digested using a multiwave 3000 microwave sample preparation system (Anton Paar, Graz, Austria) with rotor HF100 and software version v1.52. The system was equipped with 16 high-pressure PTFE-TFM vessels with an internal volume of 100 ml (maximum pressure and temperature of 40 bars and 240 °C, respectively). Typically, 0.5 g of sample, 2 mg of $^{127}$I carrier and 10 ml of 60% (v/v) $HNO_3$ suprapure quality (Merck, Darmstadt, Germany) were introduced into the vessels. The operational conditions and the heating program used were carried out according to these conditions: 200 °C for 10 min (ramp of 10 min), 200 °C for 20 min and 20 min for cooling to room temperature. The known biophilic nature of iodine [27] suggests that much of its concentration presented in soils and sediments will be associated to organic phase. Nitric acid is a strong oxidizing agent and is widely used for liberating trace elements from biological and botanical matrices because it behaves ideally under microwave conditions [28]. In the closed container, nitric acid reaches 200 °C at about 20 min. This temperature is more than 50 °C above its boiling point. At this elevated temperature, substantial increases in oxidation potential are achieved, avoiding the use of other acids (HF, HCl, etc.). After digestions, the following chemical separation consisted in an organic compound extraction followed by an aqueous solution extraction (see Fig. 1) and is based in the fact that iodine has a strong tendency to be absorbed by organic compounds [29].

### 2.2. Extraction with organic solvent

Iodine was extracted from digested samples for three times with 12 ml $CHCl_3$ and then back-extracted into aqueous solution by addition of 20 ml 0.1 M $NaHSO_3$. This compound reduces all iodine species to iodide, retaining it in the aqueous phase and avoiding its evaporation [30]. Then the solution was stirred and disturbing $SO_3{}^{2-}$ and $SO_4{}^{2-}$ ions were precipitated by addition of 10 ml of saturated $Ba(NO_3)_2$ solution followed by centrifugation. Finally, iodine was precipitated as AgI by adding 10 ml 0.1 M $AgNO_3$ solution, washed twice with distilled water and dried at 60–80 °C. The AgI was mixed with about the same volume of Ag powder and loaded in a copper target holder for the measurement of $^{129}$I at CNA. The $^{129}$I content of the sample can be calculated from the measurement of isotopic ratio $^{129}I/^{127}I$, because the added amount of $^{127}$I carrier is known.

Samples used for $^{127}$I ICP-MS measurements were prepared following the same radiochemical procedure avoiding the addition of $^{127}$I carrier and selecting iodine in the form KI (by the addition of KOH) instead of AgI in the precipitation step. The selection of this new chemical form was made because two reasons: (i) to have reference materials in the same matrixes as standard samples and (ii) because a high solubility salt was needed to dilute it in distilled water for $^{127}$I ICP-MS measurements. After cleaning with 10 ml of saturated $Ba(NO_3)_2$ solution, 10 ml KOH solution 47% pro-analysis quality (Merck, Darmstadt, Germany) was added and the solution was evaporated to dryness. Resulted KI was diluted in adequate volume of Milli-Q water (100 ml or 600 ml, depending on $^{127}$I sample content) to obtain maximum $^{127}$I concentrations in the order of 20 $\mu g\,l^{-1}$.

## 3. Measurement of $^{127}$I by ICP-MS

### 3.1. Instrumentation and instrumental settings

A quadrupolar inductively coupled plasma mass spectrometer (Thermo X7, Thermo, Madrid, Spain) equipped with a concentric quartz nebulizer (Meinhard Associates, Golden, USA) was used for $^{127}$I determination. The instrument was used at normal resolution and set to detect the signal intensity at $m/z$ 127. Samples were analyzed using some recommendations provided by US EPA 200.8 methodology adapted for iodine, although this method does not provide a procedure for determination of this element [31]. Various data quality tests were used during every instrumental running, such as replicate, matrix matching, memory effects, and both digestion analysis and laboratory reactive blanks checking. Instrumental performance optimization, including nebulizer gas flow rate, RF power and ion lens voltages, was performed and operational conditions are described in Table 1.

The instrument, located at the Servicio de Investigación Agraria laboratory (University of Seville, Spain), was used with a glass nebulizer Meinhard type, a silica impact bead spray chamber, cooled to 3 °C by a Peltier cooler, and a standard silica torch. Standard nickel sample and skimmer cones were used.

The ion optics were tuned to optimise the sensitivity of the signal at $m/z$ 9, 59, 115, 140, 137 and 238 for a 100 $mg\,l^{-1}$ beryllium, cobalt, indium, cerium, barium and uranium solution, respectively, which was typically 10,000–60,000 $counts\,s^{-1}$ in standard mode. The relative standard deviation of isotopes signals was less than 5%. The oxide and double charged levels were both monitored to ensure the $^{140}Ce^+/^{140}Ce^{16}O^+$ and $^{137}Ba^+/^{137}Ba^{++}$ ratios did not exceed 2% and 5%, respectively.

**Table 1**
Instrumental settings and calibration for ICP-MS.

| | |
|---|---|
| ICP-MS instrument | |
| Forward power | 1320 W |
| Sampler and skimmer cones: | Nickel |
| Argon flow rates: | |
| Cool gas | 14.5 $l\,min^{-1}$ |
| Auxiliary | 0.75 $l\,min^{-1}$ |
| Nebuliser | 0.93 $l\,min^{-1}$ |
| Mass-to-charge ratio detected: | $m/z$ 127 |
| Lenses parameters | |
| Extraction lens | −541 V |
| Lens 1 | 3.8 V |
| Lens 2 | −25.9 V |
| Lens 3 | −195.3 V |
| Pole bias | 6.0 V |
| Acquisition parameters | |
| Number of sweeps | 60 |
| Channels per mass | 1 |
| Dwell time | 10 ms |
| Number of main runs | 3 |
| Uptake time | 50 s |
| Wash time | 120 s |
| Calibration | |
| Type | Standard additions |
| Working standard solution | 1 $\mu g\,l\,ml^{-1}$ as potassium iodide |
| Added volumes | 100 ml and 600 ml (variable) |

The internal standard were composed by indium and terbium diluted (50 $\mu g\,l^{-1}$) in deionised water (18 MΩ cm) produced in a Milli-Q apparatus. This water was used as wash solution, with a 120 s washout time between samples (extended from the normal 50 s to prevent carryover of iodine).

Following US EPA 200.8 recommendations, nine samples were made up as standards for calibration (included calibration blank) in the ranges 0.1–20 $\mu g\,l^{-1}$ of iodine. This range was selected because two reasons: (i) because maximum $^{127}$I concentration in samples was expected to be within this range and (ii) to avoid memory effects (observed up to 100 $\mu g\,l^{-1}$ in this instrument). These standards were made by successive dilutions with deionised water (18 MΩ cm) produced in a Milli-Q apparatus (Millipore Co., Bedford, MA, USA) of an aqueous stock solution at 1000 $\mu g\,l^{-1}$ prepared from suprapure potassium iodide (Merck. Suprapure Kaliumiodid Potassium Iodide. 99.995%). A calibration curve of $^{127}$I signal obtained in Elemental and Pulse-Counting modes versus $^{127}$I concentration was then used for quantification of $^{127}$I after radiochemical extraction. The linear range of the calibration curve in shown in Fig. 2.

Instrumental detection limit of $^{127}$I calculated as three times the standard deviation of the blank [32] was 0.015 $\mu g\,l^{-1}$. Limit of quan-

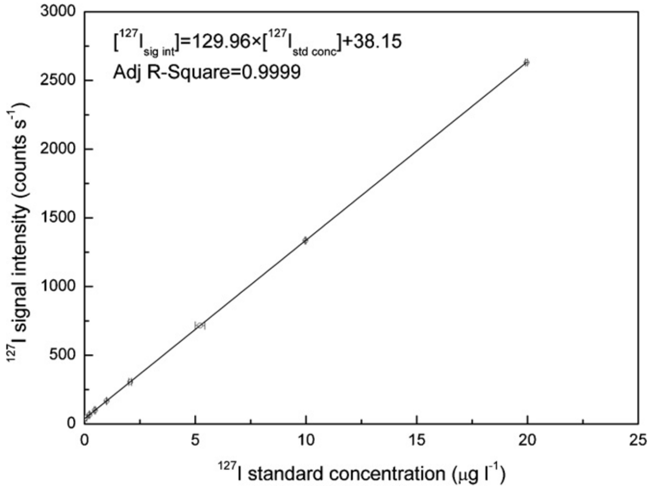

Fig. 2. ICP-MS signal intensity obtained.

**Table 2**
Results for $^{127}$I content, using ICP-MS, in certified reference materials. The uncertainty is based on one standard deviation confidence value ($n = 3$). Results found in literature are given for comparison.

| Standard reference material | | $^{127}$I content (μg g$^{-1}$) | | | |
|---|---|---|---|---|---|
| | | Certified[a] *(information)* | Measured | Reference | Determination method |
| BCR 186 | Pig Kidney | *(0.13–0.15)* | 0.13 ± 0.01 | This work | ICP-MS |
| | | | 0.13 ± 0.02 | [20] | ICP-MS |
| | | | 0.16 | [33] | ICP-MS |
| | | | 0.13 ± 0.02 | [22] | ICP-MS |
| NIST 1547 | Peach Leaves | *(0.3)* | 0.27 ± 0.02 | This work | ICP-MS |
| | | | 0.32 ± 0.02 | [1] | ICP-MS |
| | | | 0.37 ± 0.03 | [34] | RNAA |
| | | | 0.31 ± 0.03 | [12] | RNAA |
| NIST1573a | Tomato Leaves | *(0.85)* | 0.77 ± 0.08 | This work | ICP-MS |
| | | | 0.84 ± 0.04 | [1] | ICP-MS |
| | | | 0.83 ± 0.15 | [34] | RNAA |
| NIST 1549 | Non-Fat Milk Powder | 3.38 ± 0.02 | 3.10 ± 0.03 | This work | ICP-MS |
| | | | 3.31 ± 0.08 | [35] | ICP-MS |
| | | | 3.37 ± 0.25 | [36] | ICP-MS |
| | | | 3.26 ± 0.10 | [1] | ICP-MS |
| | | | 3.33 ± 0.42 | [34] | RNAA |
| | | | 3.29 ± 0.09 | [37] | ICP-MS |
| IAEA 375 | Soil from Chernobyl | 1.91 ± 0.28 | 1.75 ± 0.07 | This work | ICP-MS |
| | | | 1.78 ± 0.14 | [7] | ICP-MS |
| | | | 1.70 ± 0.12 | [4] | IC |
| | | | 1.78 ± 0.06 | [2] | IC |
| NIST 2704 | Buffalo River Sediment | *(2)* | 1.74 ± 0.02 | This work | ICP-MS |
| | | | 1.76 ± 0.07 | [2] | IC |
| NIST 2711 | Montana Soil | *(3)* | 2.77 ± 0.01 | This work | ICP-MS |
| | | | 2.67 ± 0.09 | [2] | IC |
| NIST 1648 | Urban Particulate Matter | *(20)* | 16.93 ± 0.09 | This work | ICP-MS |
| | | | 14.6 ± 0.7 | [38] | ICP-MS |
| IAEA SL-1 | Lake Sediment | *(28)* | 25.72 ± 0.08 | This work | ICP-MS |

[a] Certified and reference values are from Certificates of Analysis.

tification of iodine was 0.055 μg l$^{-1}$. Since $^{127}$I in a 0.5 g amount of sample was dissolved in 100 ml or 600 ml of Milli-Q water (depending of its iodine concentration), the limit of detection based on dry mass range from 0.003 μg g$^{-1}$ to 0.018 μg g$^{-1}$, respectively.

### *3.2. Results*

There are several standard organic and inorganic reference materials for $^{127}$I. Thus, nine reference materials were selected to check the accuracy and chemical recovery of the present method. The obtained results are listed in Table 2 together with the certified or reference values and results found in literature for comparison. Uncertainties listed defined one standard deviation of the average values. The values determined in this work agree well with certified, indicative and other published results. $^{127}$I determined concentrations range from 0.67 μg l$^{-1}$ (0.13 μg g$^{-1}$ dry mass, 0.5 g sample mass) for BCR 186 Pig Kidney to 26.16 μg l$^{-1}$ (25.72 μg g$^{-1}$ dry mass, 0.5 g sample mass) for IAEA SL-1 Lake Sediment.

Recoveries for all materials have an average value of 90%. The good agreement between measured concentration and certified (reference) values for $^{127}$I content is shown in Fig. 3. Iodine losses of 10% during chemical extraction can be due to its volatilization as HI or $I_2$ in acid means [22,39]. Incomplete digestions were found in inorganic samples (sediments and soils) but, as there were no significant differences in recoveries between organic and inorganic samples, iodine losses due to these incomplete digestions could be discarded.

From the results, it was demonstrated that the present extraction method provided samples giving satisfactory results for ICP-MS determination of $^{127}$I in some kind of environmental samples with a correlation coefficient > 0.99.

In order to check reproducibility of the extraction method (microwave digestion + chemical iodine extraction), these samples were analyzed three times. The results of the replicates are shown in Fig. 4. No large difference was found among them. The typical relative standard deviation (RSD) of each value was 6%.

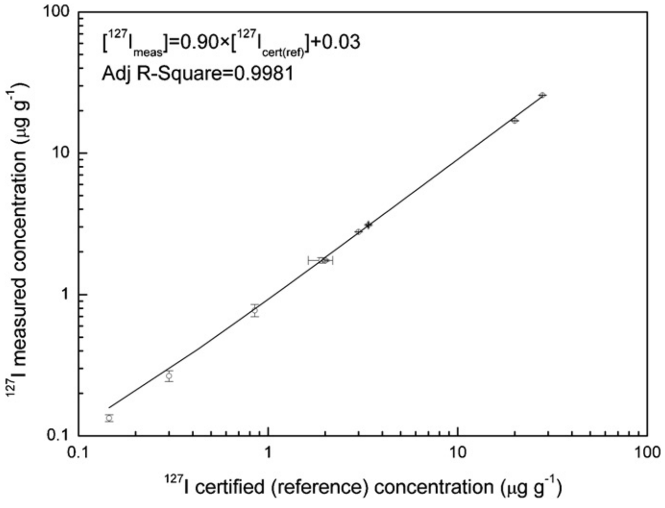

**Fig. 3.** Measured values versus certified (reference) values for $^{127}$I content. Bars show one sigma standard deviation of three data for each sample. The slope of the regression curve gives the average value of the chemical recovery.

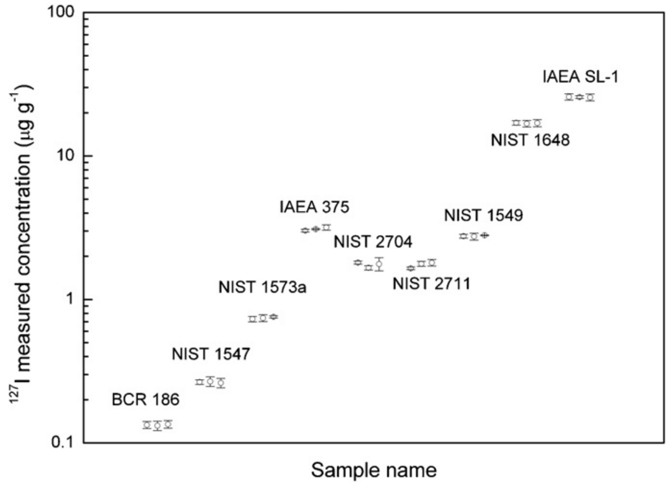

**Fig. 4.** Results of replicates for $^{127}$I concentration in different SRMs by ICP-MS. Bars show one sigma counting error.

The average RSD among three determined values (reproducibility) was 4%.

## 4. Measurement of iodine-129 by AMS

### 4.1. Experimental system

Determination of $^{129}$I/$^{127}$I ratios in the samples was conducted at the new CNA tandem accelerator (1 MV Tandetron, High Voltage Engineering Europe, Holland). The facility has been previously described [40,41], so only a short description will be given here. The low and high-energy magnets have been designed to support the analysis of heavy elements such as $^{129}$I and Pu isotopes. The high-intensity Cs$^+$ sputtering ion source is equipped with a carousel with capacity for 200 samples. Argon gas is used as stripper. The final detection of the particles is performed with a two-anode gas ionization chamber provided with a 75 nm thickness 8 mm × 8 mm silicon nitride entrance window and isobutene as counting gas. A beam of negative iodine ions was extracted from the AgI + Ag target contained in copper holders using the Cs$^+$ high-intensity sputter source at 35 keV. Typical $^{127}$I-currents at the low-energy side range from 1 to 5 $\mu$A. At the terminal of the tandem (1 MV) negative iodine ions are changed to positive iodine ions by the stripper (pressure at $6 \times 10^{-3}$ mbar of argon, which corresponds to a mass thickness of about 0.15 $\mu$g cm$^{-2}$) which are then further accelerated. Following acceleration, selected positive ions (charge state 3+) are analyzed by mass spectrometer. The $^{127}$I current beam is measured in a Faraday cup, and $^{129}$I$^{3+}$ ions are counted in the gas ionization chamber.

AMS measurements were performed relative to a standard with known $^{129}$I/$^{127}$I isotopic ratio. The used $^{129}$I standard was made by repeated dilutions from NIST SRM 3230 Iodine Isotopic Standard Level I, with a certified $^{129}$I/$^{127}$I ratio of $(4.920 \pm 0.062) \times 10^{-10}$. This standard is named $Q_1$ and its nominal ratio is $(4.66 \pm 0.02) \times 10^{-11}$. Background effects were evaluated through frequent digestions of iodine blanks, which measured a $^{129}$I/$^{127}$I isotopic ratio of $(3–4) \times 10^{-13}$ when 2 mg carrier was used. The $^{129}$I/$^{127}$I values of the samples were 70-800 times higher than this blank value thus resulting in negligible (<2%) background correction. Memory effects were evaluated analyzing samples with having $^{129}$I/$^{127}$I ratios of $\approx 1 \times 10^{-8}$. Immediately following this we analyzed a sample which had previously given a value of $(4.5 \pm 0.2) \times 10^{-11}$ and found a value of $(3.9 \pm 0.3) \times 10^{-11}$. From this we deduced that the memory effects and cross-contamination between samples was less than $6 \times 10^{-4}$.

**Table 3**
$^{129}$I concentration obtained on the CNA AMS facility for three reference materials provided by the IAEA. Errors correspond to one sigma standard deviation of three data for each sample.

| Sample | $^{129}$I concentration ($\times 10^8$ at./g) | | Reference |
|---|---|---|---|
| | This work | Certified (recommended) | |
| IAEA-375 | 11.1 ± 0.8 | 12.1 ± 2.9 | [42] |
| IAEA-414 | 65.5 ± 4.2 | (69.0 ± 0.7) | [43] |
| IAEA-437 | 5.3 ± 0.2 | (5.7 ± 0.7) | [44] |

### 4.2. Results

The viability of the technique for the measurement of $^{129}$I in environmental samples at the CNA was checked through its application to three reference materials supplied by the IAEA: IAEA-375, a soil sample from Chernobyl; IAEA-414, a mixed fish from the Irish Sea and North Sea, and IAEA-437, a Mediterranean mussel. Among these materials, only IAEA-375 has been certified for $^{129}$I concentration. The other two materials give recommended values for $^{129}$I concentration. All samples were processed according to the chemical procedure described below. The obtained AMS results are given in Table 3. In every case there was a very good agreement between the certified (recommended) values and the obtained results.

## 5. Conclusions

The validation of the proposed iodine extraction method showed average chemical recoveries of 90% for nine standard reference materials in different environmental matrices. The obtained results for $^{127}$I concentration by ICP-MS agree well with the certified/reference values and with other published results, showing iodine losses of only 10% during chemical extraction that could be due to its partial volatilization as HI or $I_2$ in acid means [22,39].

The viability of the AMS technique for the measurement of $^{129}$I in environmental samples at the CNA was fully validated by measuring $^{129}$I concentration in three IAEA reference materials. Obtained results for $^{129}$I concentration were in very god agreement with certified or reference values.

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