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Determination of environmental gaseous ^{129}I trapped in charcoal cartridges by ICP-MS/MS

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Abstract

For environmental monitoring and radioecological studies, organic and inorganic ^{129}I is often trapped in active charcoal. The analysis of this radionuclide can be difficult because of the low-level activities involved and its physico-chemical properties (e.g., volatility and multiple oxidation degrees). This study proposes a new method for ^{129}I analysis by ICP-MS/MS, which consists in the extraction of iodine from charcoal by acid digestion followed by purification using a commercial specific resin. This new method allows reaching environmental levels of gaseous ^{129}I near the fuel reprocessing plant of La Hague (France) with a limit of detection of only 2 mBq sample⁻¹.

Keywords

Active charcoal, ^{129}I , ICP-MS/MS, radiochemical treatment

Introduction

^{129}I is the radioisotope of iodine with the longest half-life ($t_{1/2} = 16.1 \times 10^6$ y [1]). This isotope is naturally produced by ^{238}U spontaneous fission or cosmic-ray spallation of Xe isotopes. It is also a nuclear fission product of ^{235}U and ^{239}Pu . This radionuclide is therefore chronically released by the nuclear industries, mainly by fuel reprocessing plants (e.g., Orano La Hague, France), in the marine environment and in the atmosphere. Moreover, gaseous or particulate ^{129}I can be released from sea to land under many forms [2, 3]. For environmental monitoring, organic and inorganic gaseous iodine are often sampled using charcoal cartridges [4, 5], often containing 20 g of charcoal to sample iodine following a filtration of 1500 to 150 000 m³ of air [6]. Most of the trapped iodine in these charcoal samples is inorganic (e.g., I₂, HOI, ...).

^{129}I is often determined by γ -spectroscopy by direct measurement or after an adapted chemical extraction [7–11]. This measurement technic is efficient and can have a short turnaround time but does not always allow reaching environmental activities of ^{129}I with a limit of detection (LOD) of 0.5 mBq g⁻¹ [12] or providing the isotopic ratio ($^{129}\text{I}/^{127}\text{I}$) determination. AMS

56 (Accelerator Mass Spectrometry) is also used for ^{129}I measurement after a chemical treatment
57 of charcoal [13]. In fact, this technic allows the quantification of ^{129}I and $^{129}\text{I}/^{127}\text{I}$ with very
58 low limits of detection (10^{-9} Bq and 10^{-13} respectively) [14, 15]. Nevertheless, even if AMS
59 performances no longer have to be demonstrated (excellent sensibility and selectivity), this
60 device is not easily accessible because of its price and its dimensions.

61 ICP-MS (Inductively Coupled Plasma – Mass Spectrometry) is an efficient and affordable
62 alternative for ^{129}I and $^{129}\text{I}/^{127}\text{I}$ determination [16–18]. However, iodine extreme volatility
63 generates memory effect [19, 20] and spectral and non-spectral interferences disturb the
64 measurement. To apply this method to gaseous iodine measurement, a chemical treatment is
65 essential before the ICP-MS/MS measurement.

66 For solid samples, as charcoal, an extraction step of iodine is indeed necessary. Oxygen
67 combustion [21] and microwave digestion [22–24] are both very efficient, but do not enable
68 the treatment of a large quantity of sample. Even if 40 g of sample can be processed with
69 alkali fusion [25–27], this method could induce about 30 % iodine loss. Pyrolysis [28–30] and
70 acid digestion in closed system, to oxidize some forms of iodine [31], are often used, allowing
71 treating 10 to 200 g of sample, and providing high-level extraction recoveries (about 90 to
72 100 %). Moreover, acid digestion is easily manufacturable in every laboratory.

73 Moreover, the purification step can ensure the reduction of the limit of detection by the
74 potential concentration of the sample and the elimination of some compounds which could
75 affect the measurement of iodine (*e.g.* salt or interferents) [32]. Liquid–liquid extraction is the
76 most used technique but requires the handling of organic solvents such as CCL_4 and TMAH
77 [9, 26, 33]. To avoid the use of such solvents, solid phase extraction [34] and ionic
78 chromatography [35–37] are also used. However, the compatibility between the separation
79 and the measurement media in ICP-MS must be previously studied.

80 The aim of this study is to propose a new method for the chemical treatment of charcoal in
81 order to determine ^{129}I and $^{129}\text{I}/^{127}\text{I}$ by ICP-MS/MS. This method consists of an acid
82 digestion followed by a solid phase extraction allowing to reach a consistent with ^{129}I
83 activities observed around Orano La Hague. I_2 is of course formed during the extraction
84 process, so it is important to use a closed system to avoid losses and trap iodine in an adapted
85 solution. The extraction step was optimized by a design of experiments (DoE) approach to
86 minimize the number of experiments while maximizing the number of studied factors. This
87 extraction is followed by a purification using the CL resin (Triskem int.). This resin, usually
88 used in LSC (Liquid Scintillation Counting), was adapted to ICP-MS/MS measurement.
89 Behaviors of ^{129}I interferences on the resin were also studied.

90 Then, the method was applied to ^{129}I determination in charcoal samples sampled in the
91 environment of Orano la Hague and allows to reach a limit of detection of $2 \text{ mBq sample}^{-1}$.

92 **Materials and methods**

93 Reagents

94 HNO_3 , H_2SO_4 NaOH and NaI used in this study are analytical grade provided by VWR BDH
95 Chemicals. Na_2CO_3 , NH_4SCN and AgNO_3 NORMAPUR™ quality are from VWR BDH
96 Prolabo®.

97 Analytical grade 60-64% Na₂S, Tween® 20 and 60-64% extra pure ferrous sulphate are
98 provided by Acros Organics™.

99 All dilutions are done with ultrapure water (18.2 ΩM cm, Merck Millipore).

100 For this study, ¹³¹I standard, I131ELSB45 (636 Bq.kg⁻¹ in 50 µg.g⁻¹ of NaI and 50 µg.g⁻¹ of
101 Na₂S₂O₃ solution), was supplied by ORANO LEA (Tricastin, France) to evaluate the
102 chemical yield.

103 Ar and O₂ gas are from Air Products with a purity of 99.999 %.

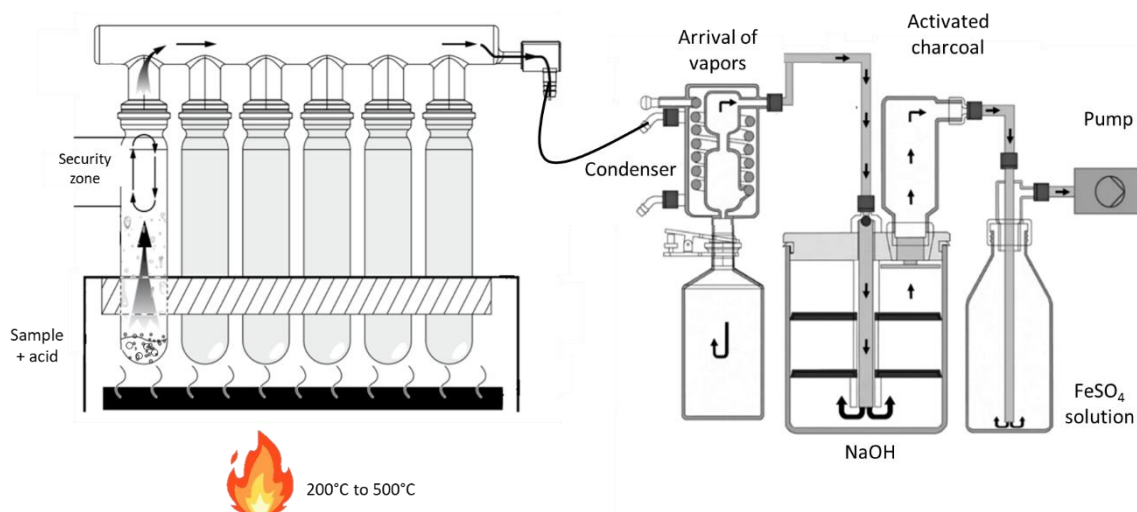
104 Samples

105 For the method development, water solutions containing 0.4 Bq in 1 mL of ¹²⁹I were prepared.

106 To verify the accuracy of the method, active charcoal samples containing ¹²⁹I collected near
107 Orano La Hague reprocessing plant, on the PTILH (49.694°N, -1.8733°W), was analyzed.
108 Organic and inorganic ¹²⁹I was sampling thanks to a High Volum Sampler at 60 m³ h⁻¹ during
109 approximately 15 days. In this study, two different charcoals were used. At the top of the
110 column, extra pure charcoal provided by Merck was used, allowing to trap gaseous inorganic
111 iodine. The TC-30 charcoal, impregnated with TEDA (triethylenediamine) provided by Hi-Q
112 was then placed to trap gaseous organic iodine [5].

113 Instrument

114 Digestion was performed using a homemade modified BÜCHI speed digester K-425 and
115 scrubber B-414 (BÜCHI Sarl), which is represented in fig. 1.



116

117

Fig. 1 – speed digester K-425 and scrubber B-414 (BÜCHI Sarl) [38, 39]

118 ¹²⁹I and ¹²⁷I are measured using the Agilent 8900 ICP-QQQ in mass-shift mode (Agilent
119 Technologies) and based on the experimental parameters proposed in a previous work for ¹²⁹I
120 and ¹²⁹I/¹²⁷I measurement by ICP-MS/MS in water samples [40]. Parameters are summarized
121 table 1:

122

Table 1 - Experimental parameters of the ICP-MS/MS

RF power	1520 W
----------	--------

RF matching	2.30 V
Sampling depth	5.3 mm
Nebulizer gas flow rate	1.05 L min ⁻¹
Solution uptake rate	1.2 mL min ⁻¹
Spray chamber temperature	0°C
Extraction lens 1; 2	-29.3 V; -205.5 V
Deflect	8 to 13 V
Energy discrimination	-8 to -4 V
Axial acceleration	0 V
Plate bias	-110 to -50 V
Octupole bias	-25 to -20 V
Cell entrance	-75 to -5 V
Cell exit	-135 to -120 V

123

124 Monitored m/z are 126, 127, 129, 130, 142, 143, 145 and 146 to follow ¹²⁶Te⁺, ¹²⁷I⁺, ¹²⁹I⁺,
125 ¹³⁰Te⁺ and their oxides forms. Indeed, Te is used as internal standard to correct signal
126 variation during ICP-MS measurement. For each sample injection, 5 replicates are performed,
127 with 300 sweeps replicates. Daily tuning is realized with a 100 µg L⁻¹ ¹²⁷I solution.

128 Purification method

129 For this study, liquid chromatography, more specifically solid phase extraction was selected
130 to purify the obtained solution after acid digestion and to preconcentrate it.

131 CL resin, commercialized by Triskem international, was used in this study. The resin consists
132 of porous microspherical beads of 100-150 µm, composed of a phosphine sulfide derivative.
133 The CL resin is based on a selective extraction system for platinum group metals, gold and
134 silver in acidic medium. In this protocol, the resin is first loaded with Ag⁺ ions to form R-Ag⁺.
135 Then, the sample is loaded onto the resin and iodide is retained by forming the AgI compound
136 [41].

137 After several rinses described by Zulauf *et al.* in their study [41], iodine is eluted from the
138 resin with Na₂S 0.35 M since the solubility product of Ag₂S is lower than that of AgI. The
139 iodide ions will therefore no longer be retained on the resin and are substituted by sulfide ions
140 S²⁻.

141 To improve this purification step, the end of fixation volume and the resin binding capacity
142 will be studied to obtain an optimized chemical yield. Moreover, tests will be carried out to
143 adapt media at the end of the previous extraction and the purification. Adjustments will be
144 made to improve the purification yield.

145 **Results and discussion**

146 Extraction of iodine

147 a) In-house adaptation of the extraction step

148 In order to obtain the best limit of detection, a large quantity of charcoal has to be analyzed.

149 Acid digestion is a very efficient technique to get a sample size > 10 g.

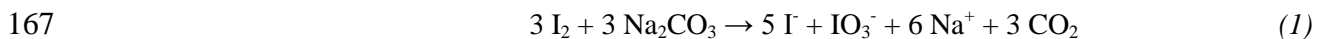
150 The BÜCHI® company has developed a fast mineralization system which also ensures the
151 neutralization of acid vapors for many applications.

152 This system, the SpeedDigester K-425, allows a rapid transfer of heat from the infrared
153 resistors to the samples (Fig.1). The heating time is therefore reduced to less than one hour
154 and the cooling is fast.

155 Several tubes can be inserted in this device; 6 tubes of 300 ml or 5 tubes of 500 ml, which
156 allows to take a large quantity of sample. Indeed, 5 to 10 g of sample can be introduced in
157 each tube, which means that up to 60 g could be introduced into the system.

158 To perform the iodine extraction step in this study, the SpeedDigester K-425 system was
159 therefore adapted.

160 For this purpose, only the suction pump of the Scrubber B-414 and the ferrous sulfate solution
161 container were used to avoid acid vapors induced by the use of nitric acid. The operating
162 principle of the acid digestion is based on the form change of iodine in acidic medium, an
163 oxidizing medium. Indeed, iodine will be oxidized to a gaseous form, I₂, and will thus be
164 extracted from the sample. To improve the efficiency of this step, the sample/acid mixture is
165 heated with a controlled temperature. In the modified system, the gas will be directed toward
166 Na₂CO₃ with a pump, where it will be trapped according to the equation 1:



168 Vapors containing gaseous iodine are successively directed to a first bubbler, then a second
169 one in order to prevent a possible saturation of the first one and finally toward a ferrous
170 sulfate solution to neutralize the potential nitrous vapors.

171 The modified system is illustrated in Fig.2:

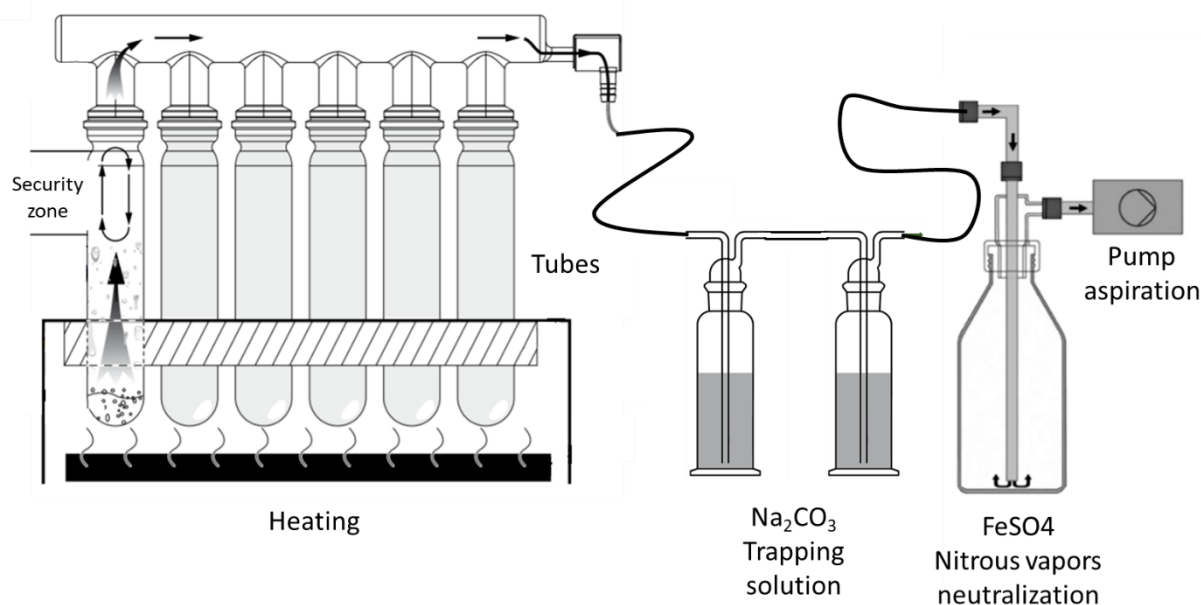


Fig. 2 - Modified system for acid digestion

172

173

174 Many parameters can influence the extraction yield obtained with this method. These
 175 parameters are:

- 176 - acid concentration;
- 177 - volume of acid;
- 178 - concentration of Na_2CO_3 ;
- 179 - volume of Na_2CO_3 ;
- 180 - pump flow rate;
- 181 - digestion temperature;
- 182 - digestion time.

183 b) Design of experiments

184 In order to select the optimal parameters for the best extraction yield, a design of experiments
 185 was performed.

186 Experiments were performed with a synthetic solution containing 50 ml of acid and 400 mBq
 187 of ^{129}I .

188 Extraction yields were determined by ICP-MS/MS measurement of ^{129}I in mass-shift mode,
 189 with reference solutions prepared in the same medium as the trapping solution (Na_2CO_3) in
 190 each experiment.

191 To set up and operate the experimental design, Minitab[®]20 software was used. A factorial
 192 design with 7 factors (presented in Table 2) was carried out with a resolution of IV.

193

Table 2 - Factors studied for the design of experiments

N°	Parameter	Range of values
1	Pump flow rate	3, 9 and 16 L min ⁻¹
2	Acid volume	100, 200 and 300 mL
3	HNO_3 concentration	6, 7 and 8 M
4	Na_2CO_3 concentration	6, 53 and 100 mM
5	Na_2CO_3 volume	50, 70 and 100 mL

6	Temperature	250, 330 and 410 °C
7	Duration	30, 60 and 90 min

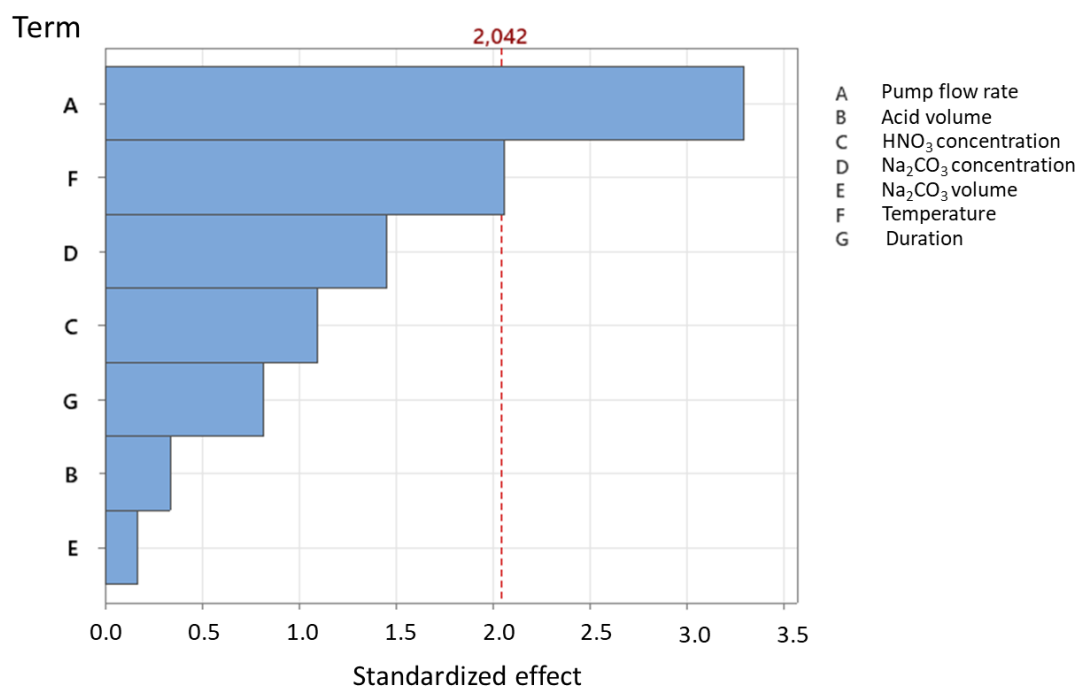
194

195 A factorial design is a type of experimental design to study effects that several factors may
 196 have on a response. When conducting an experiment, varying the levels (values) of all the
 197 factors simultaneously instead of one at a time allow studying interactions between the
 198 different factors.

199 This factorial design of resolution IV will help to determine the optimal parameters to
 200 perform an acid digestion while limiting the number of experiments carried out. Moreover, in
 201 order to avoid any contamination in the digestion system, a blank will be performed before
 202 each experiment under the same conditions. The number of experiments will thus be doubled.

203 2 double points and 3 central points are added to the 32 (2^{k-2} , with k number of factors)
 204 experiments. The double points were randomly chosen by the software to study the stability of
 205 the responses. The use of central points is indeed a very robust way to check the linearity of
 206 the model.

207 Once the experiments were performed, Minitab[®]20 was used to analyze the obtained
 208 responses. The Pareto plot (Figure 3) was generated to graphically determine the importance
 209 of the effects by ranking them from the most to the least significant, following a normal
 210 distribution.



211

212

Fig. 3 - Pareto plot of standardized effects for iodine extraction yields by acid mineralization

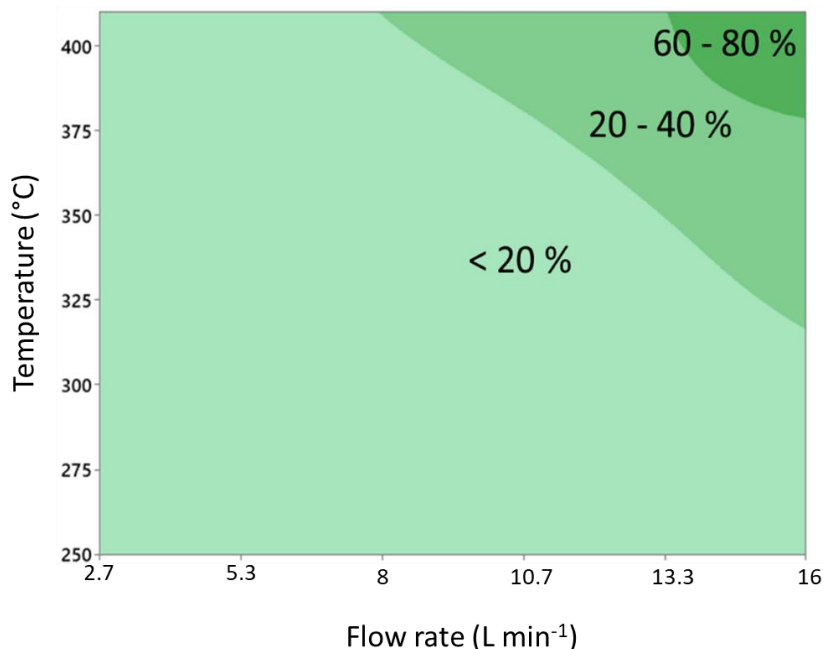
213

214 The probability of exceeding a standardized effect equal to 2.042 (the red dotted line) is
 215 97.5%. Beyond this value, the factor is considered as statistically significant.

216 In the case of the factorial design performed in this study, the factors A (pump flow) and F
 217 (digestion temperature) have a significant influence on the extraction yield. Given the chosen

218 values for the other factors (table 2), the influence they have on the extraction yield is
219 negligible.

220 A contour plot (figure 4) confirmed that flow rates and high temperatures provide a high
221 extraction efficiency, without causing an excitement of the solution.



222

223

Fig. 4 - Contour plot of iodine extraction yields by acid digestion

224 The selected parameters are summarized in table 3:

225

Table 3 - Selected parameters for iodine extraction by acid digestion

Parameter	Value
Pump flow rate	15 L min ⁻¹
Acid volume	100 mL
HNO ₃ concentration	8 M
Na ₂ CO ₃ concentration	6 mM
Na ₂ CO ₃ volume	50 mL
Temperature	410 °C
Duration	30 min

226

227 The retained acid volume is 100 mL to minimize waste as well as the risk of reaching the
228 safety zone during boiling (fig. 2). The selected acid concentration is 8 M to maximize the
229 extraction recovery. A short bubbling time (30 min) is enough to recover iodine. The selected
230 Na₂CO₃ volume was 50 mL to minimize the sample volume during the following purification.

231 However, the volume is higher than 50 mL after this extraction step (around 70 mL) and the
232 pH of the solution is acid (~ 2). To avoid iodine losses, and to stabilize iodine under I⁻ form,
233 ascorbic acid is added to the solution to have a solution of 1 % (w/v) in the bubbler (100 mM
234 Na₂CO₃). Ascorbic acid is a reducing agent that will help maintaining iodine under the form
235 of I⁻. Furthermore, pH of the bubbling solution is corrected to be > 7 using ammonia 20 %.
236 Ascorbic acid and the pH adjustment prevent the loss of 50 % of iodine at the end of this step.

237 When analyzing environmental samples, ^{131}I is added as a tracer to verify the chemical yield.
 238 ^{131}I is used as a tracer for several reasons: it is indeed easily measured by gamma
 239 spectrometry due to its high emission intensity (81.2% at 384.5 KeV [42]), and this
 240 radionuclide is not present in environmental samples because of its short half-life of 8 days.

241 Purification by Solid Phase Extraction (SPE)

242 After the extraction step, iodine is under I^- and IO_3^- forms in 50 mL of 6 mM Na_2CO_3 solution
 243 ($\sim 0.6\%$ w/v). This measurement medium is not compatible with ICP-MS/MS measurement
 244 due to the salt concentration. A purification step is necessary to adapt the medium. Moreover,
 245 the purification step could be useful for the elimination of ICP-MS interferences that have
 246 never been studied. In addition, this step will allow the preconcentration of the sample as the
 247 preconized elution volume is 5 mL.

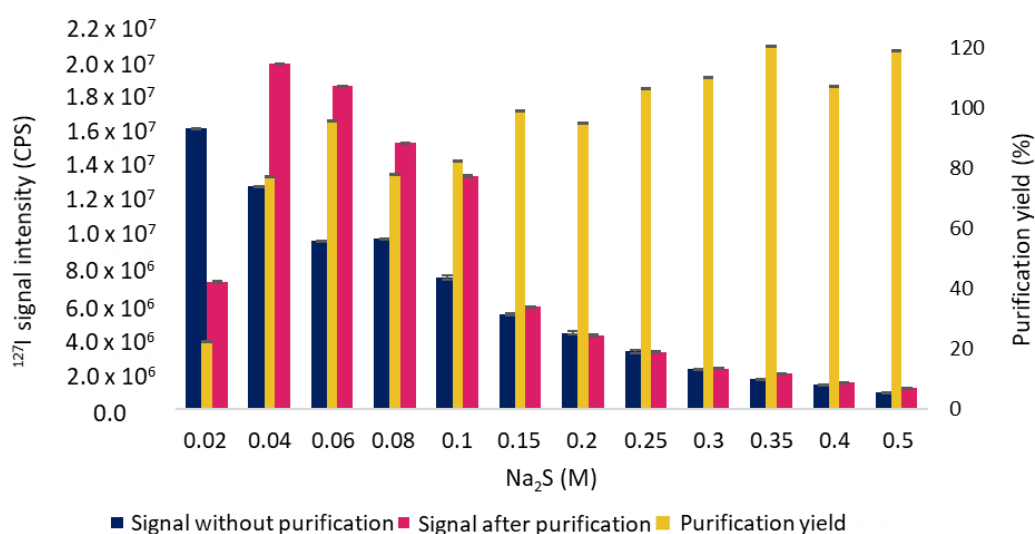
248 In order to prevent the clogging of the introduction system and to eliminate interferences before
 249 the measurement by ICP-MS/MS, a purification step of the iodine fraction was performed.
 250 This purification step will transfer iodine to a suitable medium for ICP-MS/MS measurement
 251 and preconcentrate the sample.

252 The CL resin was used in this work.

253 The purification on this resin is assisted by a peristaltic pump in order to control the flow rate
 254 which was initially fixed at 1.35 mL min^{-1} (3 rpm).

255 a) Compatibility between elution and ICP-MS/MS measurement media

256 Iodine is eluted from the CL resin with Na_2S . In order to study the compatibility of this
 257 medium with ICP-MS/MS measurement, solutions of $100 \mu\text{g L}^{-1}$ of stable iodine in different
 258 molarities of Na_2S were measured with on-mass mode. The same solutions of Na_2S
 259 containing iodine were also measured after the purification procedure. Purification yields
 260 were calculated to check the efficiency of this separation method and the compatibility of Na_2S
 261 with ICP-MS measurement. The results of these experiments are presented in Fig.5.



262

263 *Fig. 5 - Variation of the ICP-MS/MS sensitivity with different Na_2S concentrations. Uncertainties are the RSD (standard*
 264 *deviation / average) for the sensitivity before and after purification. They were determined at $k = 2$ for the yield.*

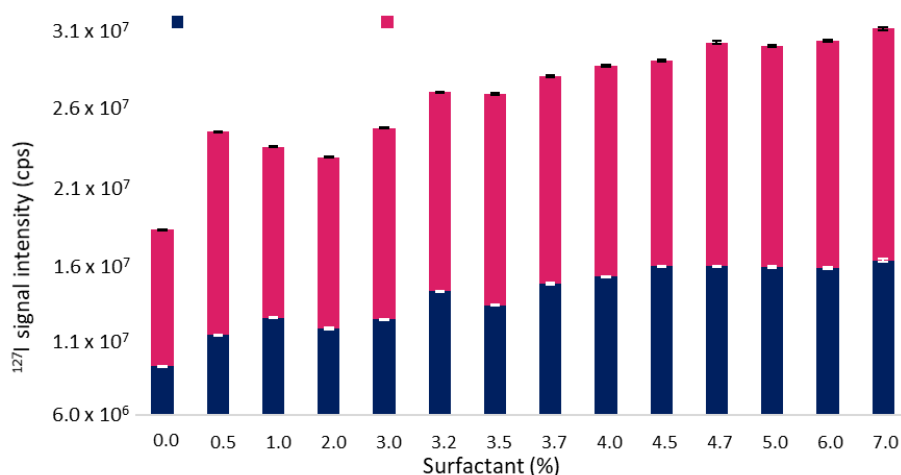
265 According to the results shown in Figure 4, the more Na₂S concentration increases, the more
266 iodine sensitivity decreases. The purification efficiency starts to exceed 75% for
267 concentrations from 0.06 M. The recommended concentration is 0.35 M [41], presenting an
268 optimal purification yield. On the other hand, at this concentration, the sensitivity is very low
269 in ICP-MS. At 0.06 M, the yield is slightly lower but the sensitivity is ~ 10 times higher. This
270 concentration allows then having the best compromise between the yield and the sensitivity.
271 Na₂S solution at 0.06 M will be used to eluate iodine from the resin in order to measure ¹²⁹I
272 by ICP-MS/MS.

273 b) Improvement of the sensitivity

274 In a previously published work, Tween[®] 20 has been used to increase sensitivity and decrease
275 memory effect when measuring iodine by ICP-MS [40].

276 Tests were carried out by adding this surfactant to the elution fraction. In order to study the
277 response, several solutions of 100 µg L⁻¹ of NaI were prepared in 0.06 M Na₂S and then
278 measured directly and after purification after addition of various quantities of Tween[®]20 in
279 the elution fraction.

280 The obtained results are presented in Fig.6.



281
282 Fig. 6 - Variation of sensitivity before and after resin passage when adding different quantities of Tween[®] 20. The error bars
283 correspond to sensitivity RSD

284 These results confirm that the addition of Tween[®]20, a non-ionic surfactant, to Na₂S solution
285 prior to ICP-MS/MS measurement improves sensitivity. The highest sensitivity is obtained for
286 a concentration of 4.7%. Therefore, in this study, this concentration will be selected for
287 measurements after purification by SPE.

288 c) Optimization of purification time

289 In order to select the flow rates that provides the best balance between separation time and
290 purification yield, 100 µg L⁻¹ solutions were prepared and purification was performed by
291 varying the flow rate, step by step, from 0.4 to 8.8 mL min⁻¹ (1 rpm steps). For each
292 experiment, the purification yields were calculated to determine the optimal flow rates. The
293 flow rate was varied to select the optimal one to have the best purification yield. Selected flow
294 rates are presented in Table 4.

295

Table 4 - Selected flow rates for sample purification with CL resin

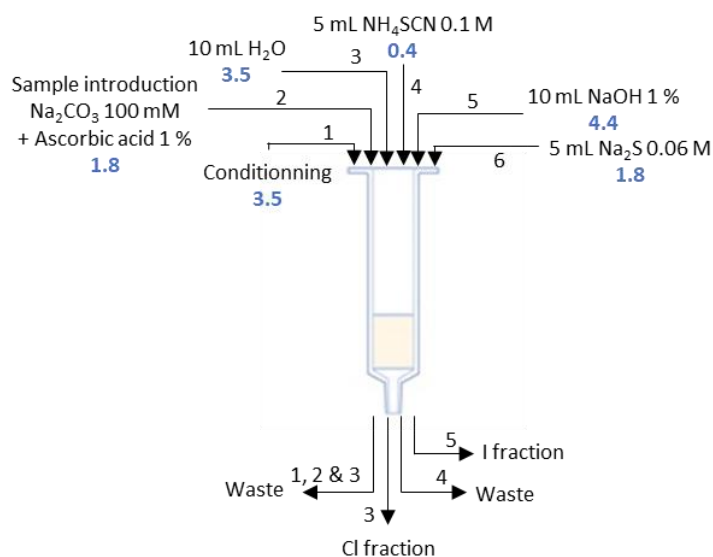
Step	Flow rate (mL min ⁻¹)
1 - Conditioning	3.5
2 - Percolation	1.8
3 - Rinse (H ₂ O)	3.5
4 - Rinse + Cl elution (NH ₄ SCN)	0.4
5 - Rinse (NaOH)	4.4
6 - Elution I (Na ₂ S)	1.8

296

297 The conditioning and rinsing steps with water and sodium carbonate can be performed with a
 298 higher flow rate than the 1.35 mL min⁻¹ used before optimization. In contrast, the ammonium
 299 thiocyanate rinse step cannot be performed with a high flow rate (more than 0.4 mL min⁻¹), as
 300 this increases the risk of substituting AgI with AgSCN and thus eluting I⁻ as NH₄I. The flow
 301 rate for iodine elution from the resin with 0.06 mM Na₂S is optimal from 0.4 to 1.8 mL min⁻¹.
 302 Above 1.8 mL min⁻¹, the time is too short to allow efficient ion exchange.

303 By optimizing the flow rates, the purification time was reduced from 1.5 hours to less than 40
 304 minutes for a 10 mL percolated sample with a purification yield of 96 %.

305 The purification step optimized for ICP-MS/MS measurement is summarized in Fig.7.



306

307 Fig. 7- Optimized purification step. The flow rates are indicated in blue (mL min⁻¹)

308 d) Study of the end of fixation volume

309 The end of fixation volume for iodine on the CL resin is the sample volume at which iodine is
 310 no longer fixed for a resin volume of 2 mL (internal diameter of 7 mm and a length of 39
 311 mm).

312 It may sometimes be necessary to purify a larger sample volume to fit the extraction volume
 313 (previous step) or to have a better limit of detection in some cases (seawater analysis for
 314 example).

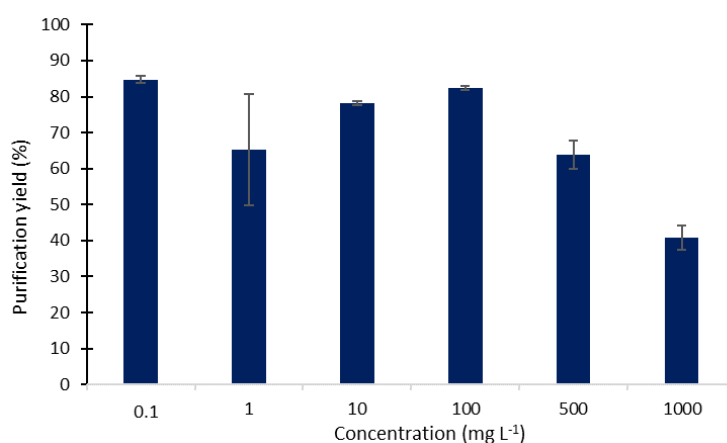
315 Tests were performed and concluded that up to 1 L of sample could be introduced into the CL
 316 resin without impacting the purification yield but only the purification duration.

317 Percolation of 1 L and elution with only 5 mL imply a preconcentration by a factor of 200.
318 Then the limit of detection with this method could be 200 times better than that presented in
319 the previous study [40], 11 mBq. The new limit of detection after a chemical treatment could
320 then reach 2 mBq.

321 e) Resin binding capacity

322 Studies by Zulauf *et al.* showed that up to 20 mg of iodine could be separated with 2 mL of
323 the CL resin and eluted with 5 mL of a 0.35 M Na₂S solution [41]. The selected
324 concentration, 0.06 M, and the modified flow rates could degrade the elution yield. To verify
325 that the changes do not degrade the elution yield for high quantities of iodine, tests were
326 performed by percolating 10 mL at different concentrations through CL resin. The obtained
327 results are presented in Fig.8.

328



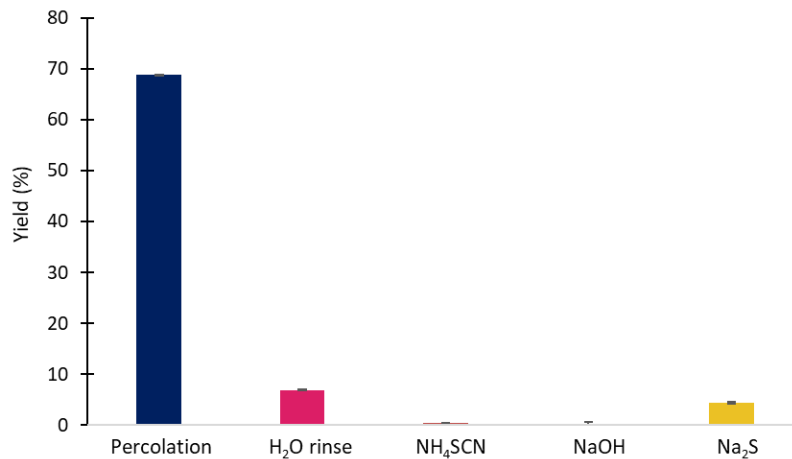
329

330 *Fig. 8- Purification yield as a function of percolated iodine concentration. The error bars were calculated at k =2.*

331 These results confirm that iodine is well fixed and eluted with 0.06 M Na₂S, for
332 concentrations up to 500 mg L⁻¹ (50 mg inserted on 2 mL of resin). These results are
333 consistent with those obtained by Zulauf *et al.* and confirm that the protocol modifications do
334 not degrade performances obtained with the CL resin [41].

335 f) Fixation of iodate ions on the CL resin

336 The calculated chemical yield after the extraction and the purification steps was initially 10 ±
337 1%. According to Eq. (1), iodate and iodide ions are formed during the extraction step. In
338 order to study the behavior of iodate ions during the following purification with CL resin,
339 tests were performed with solutions of IO₃⁻ prepared in Na₂CO₃ 100 mM. The purification
340 procedure was applied to each solution and all the fractions were collected so that iodine
341 could be measured by ICP-MS/MS. The results are presented in Fig.9.



343

344

Fig. 9- Study of the behavior of IO₃⁻ ions on CL resin

345 These results show that iodate ions are not retained on the CL resin. The solubility products of
 346 Ag₂CO₃ is indeed lower than that of AgIO₃ (Eq. (2)), so when a sodium carbonate solution
 347 containing iodate ions is inserted into the column filled with CL resin, CO₃⁻ ions preferentially
 348 form AgCO₃ compound and iodate ions are not retained.

349

$$K_{S_{Ag_2CO_3}} = 2[Ag^+] \times [CO_3^{2-}] = 10^{-12} \quad (2)$$

350

$$K_{S_{AgIO_3}} = [Ag^+] \times [IO_3^-] = 10^{-8}$$

351

g) ICP-MS interferences behavior on the CL resin

352 As the CL resin was initially designed for a liquid scintillation measurement, ¹²⁹I ICP-MS
 353 interferences behaviors during the separation step has never been studied. The polyatomic
 354 interferences of ¹²⁹I by ICP-MS are presented table 5.

355

356

Table 5 - ¹²⁹I interferences in ICP-MS [10], [14], [34,]

Element	Polyatomic interferent
Y	⁸⁹ Y ⁴⁰ Ar ⁺
Mo	⁹⁷ Mo ¹⁶ O ₂ ⁺
Cd	¹¹³ Cd ¹⁶ O ⁺
In	¹¹⁵ In ¹⁴ N ⁺ , ¹¹³ InO ⁺
I	¹²⁷ IH ₂ ⁺ , ¹²⁷ ID ⁺

357

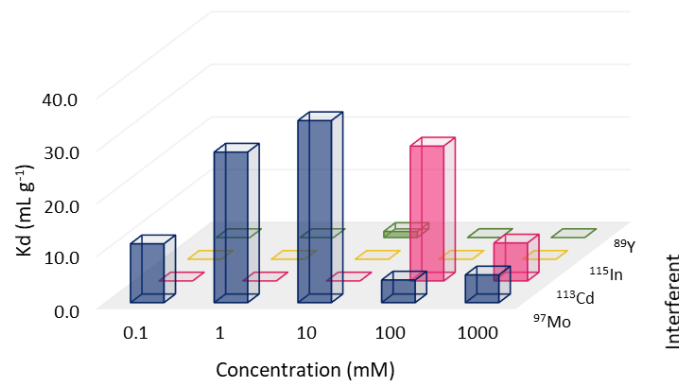
358 The distribution coefficients (K_d) have been calculated according to Eq. (3) for each
 359 interferent during iodine purification steps. This study was performed in batch where 200 mg
 360 of resin with Ag⁺ were inserted into a 25 mL beaker. 100 μg L⁻¹ of each interferent were
 361 added to 5 mL of Na₂CO₃, NH₄SCN, NaOH and Na₂S solutions ranging from 0.1 mM to 1 M
 362 and water. These solutions were stirred for 19 h. The solutions were then recovered for ICP-
 363 MS measurement by eliminating the resin using an empty column containing a filter.

364

$$Kd (ml g^{-1}) = \left(\frac{CPS_i - CPS_f}{CPS_f} \right) \times \left(\frac{V}{m} \right) \quad (3)$$

365 CPS_i and CPS_f represent the CPS (Counts Per Second) obtained by ICP-MS before and after
 366 passing through the resin. V is the volume of solution (mL) and m is the mass of resin (g).

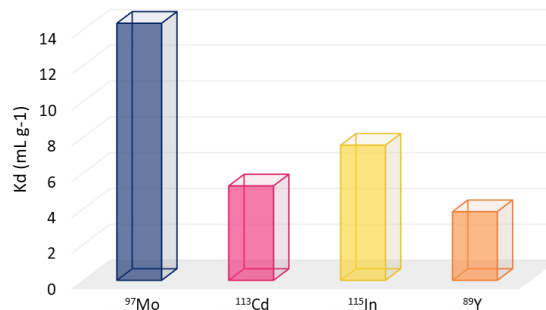
367 The calculated Kd in Na_2CO_3 , H_2O , NH_4SCN , $NaOH$ and Na_2S media are presented in the
 368 following figures:



369

370 *Fig. 10- Distribution coefficients of iodine 129 interferents on CL resin as a function of Na_2CO_3 concentration*

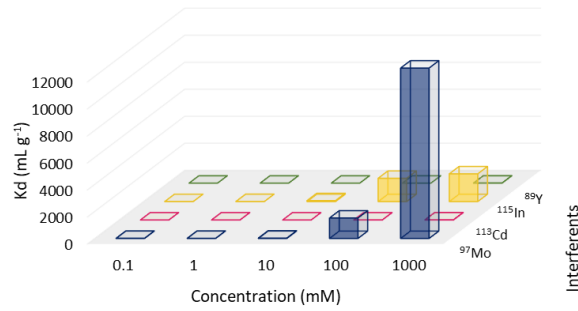
371 The sample, after the extraction step, is loaded on the resin in 6 mM Na_2CO_3 . At this
 372 concentration, Y, Cd and In are not retained on the resin. Mo, on the other hand, is relatively
 373 well retained with a $Kd > 30 mL g^{-1}$.



374

375 *Fig. 11- Distribution coefficients of iodine 129 interferents on CL resin in water*

376 The interferents are all slightly retained on the resin in water. This step does not, or only
 377 slightly, remove the previously retained interferents, but it does rinse saline load excess of the
 378 resin.

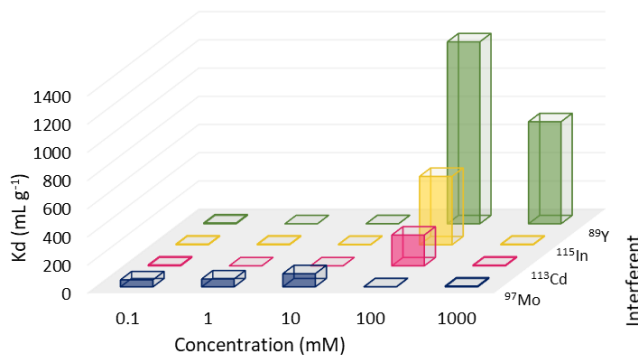


379

380

Fig. 12 - Distribution coefficients of iodine 129 interferences on CL resin as a function of NH_4SCN concentration

381 NH_4SCN concentration during sample purification is 100 mM. At this concentration, Mo and
 382 In are retained on the resin with $K_d > 2000 \text{ mL g}^{-1}$.

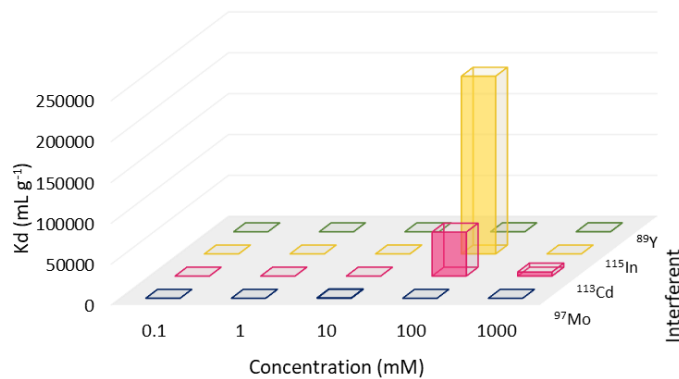


383

384

Fig. 13- Distribution coefficients of iodine 129 interferences on CL resin as a function of NaOH concentration

385 The concentration of NaOH during sample purification is 250 mM. At this concentration, Mo
 386 is not retained on the resin. Cd and In are retained on the resin, as well as Y, which is strongly
 387 retained.



388

389

Fig. 14- Distribution coefficients of iodine 129 interferences on CL resin as a function of Na_2S concentration

390 According to the figure 15, Cd and In are not retained in the resin when the concentration of
 391 Na_2S is 10 mM. However, these two elements are retained very well when the concentration
 392 is 100 mM. In this study, the concentration of Na_2S is 60 mM.

393 These results show that from the first step, Y and In are not retained on the resin in 6 mM
 394 Na₂CO₃. Then, a slight part of Cd and Mo is removed with H₂O because of the low Kd
 395 obtained in this medium.

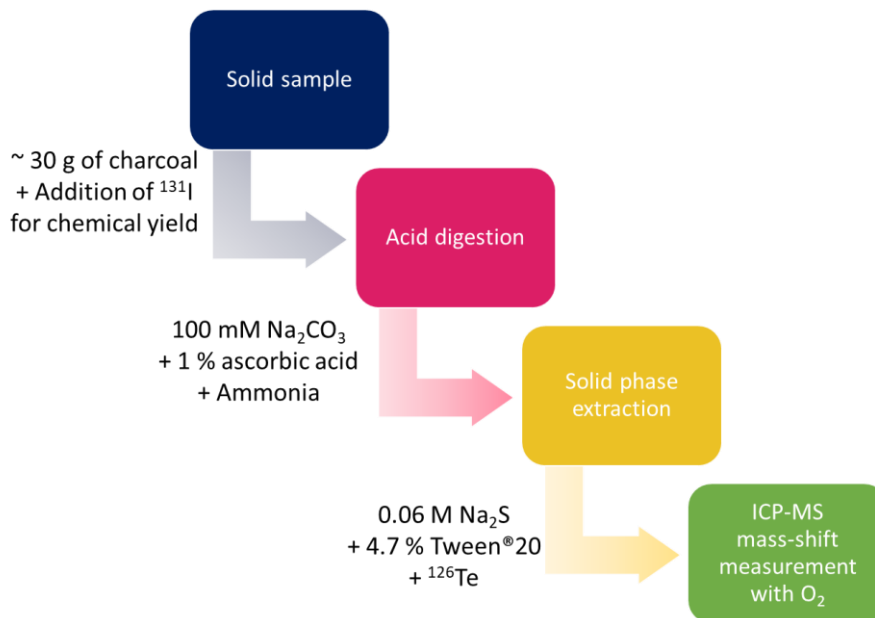
396 Part of Mo is also removed in the NH₄SCN fraction.

397 The Kd obtained for Mo in 250 mM NaOH (1%) is lower than 5. The remained Mo is then
 398 totally removed in this fraction.

399 Interferents are eliminated before the elution step with Na₂S and will therefore not be a barrier
 400 to the ¹²⁹I measurement by ICP-MS/MS.

401 Validation of the method

402 A strategy for the analysis of ¹²⁹I and ¹²⁹I/¹²⁷I in charcoal samples has been defined in the
 403 current and the previous study and summarized in Fig.15. To evaluate the chemical yield, ~50
 404 Bq of ¹³¹I were added to the sample as a tracer before the extraction step.



405

406

Fig. 15- Processing strategy for environmental samples

407 Activated charcoals are often used to trap gaseous organic and inorganic iodine. It is indeed
 408 used in environmental studies, environmental monitoring or to reduce the emission of
 409 radioactive iodine from nuclear facilities.

410 For this purpose, the treatment of activated charcoals in order to quantify ¹²⁹I at low level is
 411 an important issue. Tests were carried out by measuring ¹²⁹I trapped near Orano La Hague
 412 reprocessing plant (as described above) on cartridges containing 30 g of charcoal. Reference
 413 activities were determined by a validated and a well-established gamma spectrometry routine
 414 method. The newly developed method was applied to these samples. Bias and standardized
 415 deviations were calculated according to Eq. (4) and (5).

416

$$Bias (\%) = \left| \frac{[^{129}I]_{mes} - [^{129}I]_{th}}{[^{129}I]_{th}} \right| \times 100 \quad (4)$$

417
$$SD = \frac{|[^{129}I]_{mes} - [^{129}I]_{th}|}{\sqrt{U^2[^{129}I]_{mes} + U^2[^{129}I]_{th}}} \quad (5)$$

418 Results are presented in table 6.

419 *Table 6 – Activated charcoal after new method treatment*

Sample	Reference activity (mBq); $k=2$	Measured activity (mBq); $k=2$	Bias (%)	Standardized deviation
Charcoal 1	131.00 ± 20.00	127.00 ± 4.92	3.06	0.51
Charcoal 2	114.00 ± 19.00	101.43 ± 8.48	11.03	0.06
Charcoal 3	91.00 ± 17.00	95.53 ± 4.66	4.98	0.03
Charcoal 4	66.00 ± 14.00	75.47 ± 8.25	14.35	0.07
Charcoal 5	6.00 ± 6.00	5.29 ± 1.98	11.9	0.11
Charcoal 6	< 10.00	3.21 ± 0.08	/	/
Charcoal 7	< 7.00	5.11 ± 0.47	/	/
Charcoal 8	< 8.00	2.56 ± 0.18	/	/
Charcoal 9	< 5.5	3.02 ± 0.55	/	/

420
 421 The obtained results presented in table 5 highlight the efficiency of the ICP-MS/MS method
 422 with results consistent with the ^{129}I measurements by gamma spectrometry. Indeed, the bias
 423 are all below 15% and the standardized deviations lower than 1.

424 Unlike gamma spectroscopy, the method newly implemented by ICP-MS/MS enhance the
 425 capability to reach ^{129}I activities in charcoal 5, 6 and 7 due to its lower limit of detection. The
 426 obtained limit of detection (calculated following the currie equation [44]) after the extraction
 427 of iodine from 30g of charcoal and the purification step is 2 mBq sample⁻¹.

428 **Conclusion**

429 A new method for ^{129}I quantification in complex samples, e.g., charcoals, has been developed.
 430 This method relies on extraction, purification and measurement steps. The procedure was
 431 designed to ensure that iodine loss by volatilization is avoided. Compatibility of the media
 432 between the different analytical steps was indeed carefully studied and adapted.

433 Iodine was extracted from solid samples by acid digestion. A closed system was set up by
 434 modifying a commercial device designed to digest samples. Iodine is trapped by bubbling in a
 435 basic solution of Na₂CO₃. In order to obtain the best performances, a factorial design of
 436 experiments was carried out.

437 A solid phase extraction was then set up using CL resin. This resin was adapted to the
 438 measurement of iodine by ICP-MS/MS by optimizing the Na₂S concentration to 0.06 M for
 439 the elution step.

440 Furthermore, the purification time has been decreased from 1h30 to 40 min for a 10 mL
 441 sample volume.

442 The behavior of ^{129}I interferences in ICP-MS/MS was studied on CL resin.

443 This new method can reach limit of detection of 2 mBq sample⁻¹. This allows to reach lower
 444 iodine activities than before with radiometric technics with an optimized turnaround time
 445 (e.g., less than a day for the entire protocol).

446 The method was validated with cross analysis by gamma spectroscopy using charcoal
447 cartridges containing gaseous iodine.

448 **Conflicts of interest**

449 Authors have no conflicts of interest to disclose.

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