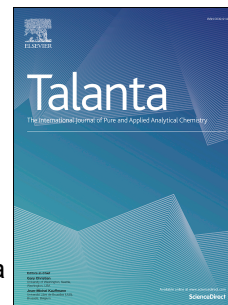# Journal Pre-proof

The use of high resolution graphite furnace molecular absorption spectrometry (HR -MAS) for total fluorine determination in extractable organofluorines (EOF)

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1   THE USE OF HIGH RESOLUTION GRAPHITE FURNACE MOLECULAR

2   ABSORPTION SPECTROMETRY (HR -MAS) FOR TOTAL FLUORINE

3   DETERMINATION IN EXTRACTABLE ORGANOFLUORINES (EOF)

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22

23   Abstract:

24   The determination of total fluorine content using high-resolution graphite

25   furnace continuum source molecular absorption spectrometry (HR- MAS) has been

26   employed in a variety of samples for over 10 years. However, most of the samples

27   analysed by HR- MAS are rich in fluoride, with negligible levels of organic fluorinated

28   species. With an increase in concern surrounding per- and polyfluoroalkyl

29   substances (PFASs), new methods to measure total fluorine of organofluorine using

30   different techniques have been developed. However, no studies focused on PFASs

31   behaviour in HR-MAS have been performed. As these compounds encompass a

32   wide range of different structures, boiling points, decomposition temperatures and

33   matrix interactions, a loss of accuracy can occur when an aqueous external

34   calibration is performed using only one compound. To overcome this issue, an

35   investigation into permanent modifiers for the graphite furnace was performed. After

36   optimisation similar sensitivity for different PFCA was achieved when 400 µg of W

37   was used as a permanent modifier together with an optimised temperature program.

38   The relative deviation between the different PFCA standard slopes relative to the

39   PFOA slope was lower than 15%. The instrumental limit of detection and

40   quantification (LOD and LOQ, respectively) of total fluorine as total PFCA was 0.1

41   mg L^{-1} and 0.3 mg L^{-1}, respectively, while the method LOD and LOQ (using solid

42   phase extraction) was 0.3 µg L^{-1} and 1.0 µg L^{-1}, respectively. The developed method

43   gave satisfactory recoveries for the spiked PFCA into seawater, river water and

44   effluent using PFOA calibration standards. The optimised method is useful for

45   measuring extractable organofluorines (EOF) when only ionic PFASs such as PFCA

46   are expected. When other organofluorines are expected, the results using HR GF-

47   MAS should be taken with caution.

48   KEYWORDS: per- and polyfluoroalkyl substances, HR-MAS, fluorine

49   determination, POP, PFAS.

50   **1. Introduction**

51   Fluorine is essential for human health. Enhance fluorine analysis in water and

52   food is mandatory. However, most common methods are actually determine only the

53   amount of fluoride such as ion selective electrode (ISE) or ion chromatography [1].

54   This is because only fluoride is known to protect from dental decay and promotes

55   healthy bones, due to its role in proper calcium mineralization and formation of

56   dental enamel [2]. The European Food Safety Authority (EFSA) recommends an

57   intake of 0.05 mg of fluoride per kg of body weight per day for children and adults [3],

58   and the World Health Organization (WHO) recommends fluoride concentrations

59   between 0.8 and 1.5 mg/L in drinking water [4]. Alongside this, humans are exposed

60   to fluoride through breathing air and foods such as dill, cucumber and pickles [5].

61   However, an excess of fluoride in the diet may cause dental or skeletal fluorosis

62   which can lead to staining and even high porosity in dental enamel, ligaments

63   calcification and bone lesions, with accumulative effects [6].

64   Besides the concern caused by excessive uptake of fluoride, humans may be

65   exposed to fluorine via organofluorine compounds, which are used extensively as

66   pharmaceuticals, anaesthetics, agrochemicals, refrigerants and industrial polymers

67   [7]. Of particular concern are per- and polyfluoroalkyl substances (PFASs) which are

68   a class of over 4000 anthropogenic chemicals containing one or more fully

69   fluorinated carbon atoms. PFASs are widely used in consumer products, including

70   cosmetics, food packaging, and textiles [8]. PFASs tend to be highly persistent and

71   accumulate in human blood globally . As opposed to most persistent organic

72   pollutants, which have been studied for a long time with well-known side-effects from

73   their indiscriminate use, investigations into the effects of PFASs are still in their

74   infancy [10]. The reason for such lack of concern about this class of compounds is

75 in the stability of C-F bound, with an average bond energy 485kJ/mol [11,12], which

76 causes many scientists to believe in a supposed lower reactivity of organofluorine

77 compounds [9]. Believed to be inert and safe, these compounds were produced on

78 an industrial scale before being considered an emerging pollutant due their non-

79 degradable and bioaccumulative properties, leading them to recently become a hot

80 topic [13]. The chronic and acute toxicities of various PFASs have been analysed

81 due to the potential threat they pose to humans and wildlife. These analyses showed

82 that PFASs demonstrate carcinogenicity, hepatotoxicity, immunotoxicity,

83 developmental toxicity and affect hormones [14]. There have also been studies that

84 show the residence time for PFASs in humans to be longer than that in laboratory

85 animals [15], leading to even greater concern over their effect on human health and

86 the need for regulation of PFASs in consumer products.

87   In 2009, perfluorooctane sulfonate (PFOS) and related PFASs were added to

88 Annex B of the United Nations Stockholm Convention on Persistent Organic

89 Pollutants, in order to reduce and eventually eliminate the use of PFASs in industry,

90 recognising PFASs as a threat to human health and the environment [16]. This

91 recognition of the need for regulation is important yet requires appropriate methods

92 of analysis to monitor. However, the measurement of PFASs is much more

93 challenging than other chlorinated and brominated compounds [17] due to the huge

94 number of structurally different chemicals. Despite the different behaviour routinely

95 only dozen of PFASs are monitored using HPLC-ESI-MS/MS in targeted analysis

96 [18]. Hence, fractionation schemes have been developed which would determine the

97 amount of total fluorine, extractable organofluorines (EOF) [19,20] to determine the

98 extent of PFASs and other organofluorines through a mass balance approach [21].

99   For total fluorine a few methods have been described in the literature such as PIGE,

100 INAA and CIC and recently compared for food packeting material [22].

101   On the other hand, spectroscopic techniques exhibit great potential for

102 application to total fluorine determination, the current methods include laser-induced

103 breakdown spectroscopy, and inductively coupled plasma mass spectrometry [23–

104 26].

105   Here in this study we focussed on the use of high-resolution molecular

106 absorption spectrometry (HR-MAS) for the determination of total fluorine. HR-MAS

107 involves the formation of a metal monofluoride such as GaF, and CaF, and the

108 measurement of its molecular absorption bands within the range of commercially

109 available AAS. This technique has been used for fluorine determination due its

110 robustness, low operational cost when compared to the plasma techniques, high

111 analytical throughput, presenting accurated results with simple or even any sample

112 preparation procedure, once optimized temperature program and permanent

113 modifier is able to remove interferences efficiently.

114   Dittrich et al. [27] investigated using HR-MAS with a graphite furnace (GF) for

115 the determination of halogens using different forming reagents such as Ga, Al, Tl, In

116 and Mg salts. Morés et al. [28] investigated the most sensitive wavelength for CaF

117 and found this to be 606.440 nm for the determination of total-F in tea which is most

118 likely only fluoride with small amounts of fluoroacetate. Other successful studies

119 have used CaF to measure the total-F content in milk and coal [29,30]. For these

120 cases, when Ca was used as the forming reagent, neither permanent (which can be

121 impregnated onto the platform surface after a temperature program) nor chemical

122 modifiers in solution (added in the graphite tube with the sample) were not used.

123   All papers mentioned above describe an analysis of total fluorine content of

124   different samples, however no studies investigating different fluorinated compounds

125   behaviour in HR-GF MAS were performed. Since an expressive part of the fluorine is

126   in the inorganic form, any loss of accuracy caused by a difference in sensitivity

127   between the inorganic standard used for calibration and the organofluorine species

128   present in the sample would be negligible. However, if an organic extraction is

129   performed, the quantification of the extractable organofluorine using external

130   calibration with inorganic standards can lead to inaccurate results, since the

131   behaviour of organofluorine in a graphite furnace remains unknown. Different boiling

132   points, decomposition temperatures and interactions with the permanent modifier

133   can occur, resulting in differences in sensitivity of the organofluorine compounds.

134   This study presents an investigation into the thermal behaviour of the most

135   common PFASs, with the development of a method able to quantify the sum of all

136   organofluorines occurring in the different classes of PFASs present in a methanolic

137   solution, as a tool for fluorine mass balance. The study was executed through the

138   application of different permanent modifiers, in order to reduce the deviation in

139   sensitivity among different PFASs. The accuracy of the developed method was

140   assessed by standard addition followed by solid phase extraction (SPE) in different

141   water samples (sea water, river water, effluent and wastewater).

142   **2. Experimental**

143   *2.1 Instrumentation*

144   A high-resolution continuum source atomic absorption spectrometer (model

145   contrAA 700, Analytik Jena, Jena, Germany) was used for all measurements. The

146   spectrometer was equipped with a xenon short-arc lamp with a nominal power of 300

147   W operating in a hot-spot mode, which emits a spectral continuum between 190 and

148   900 nm and a charge-coupled device (CCD) array detector with 588 pixels, 200 of

149   which are used for analytical purposes. The double monochromator consists of a

150   prism pre-monochromator and an echelle grating monochromator for high resolution.

151   All measurements were performed using the wavelength of highest sensitivity for

152   CaF at 606.429 nm, using the sum of the integrated absorbance of three pixels

153   (peak volume selected absorbance, PVSA, $A\Sigma3,int$) [31]. Pyrolytically coated

154   graphite tubes with PIN platform (Analytik Jena, Germany) and with transversal

155   heating were used in all experiments.

156   *2.2 Materials and reagents*

157   Ultrapure water with a resistivity of 18.2 MΩ cm (Smart2 Pure, Thermo Fisher

158   Scientific, Loughborough, UK) was used for the preparation of the standard

159   solutions. The fluorine standard was prepared from 1 g L^{-1} F from KF in water

160   (Thermo Fisher Scientific) and $Ca(NO_3)_2 \cdot 4H_2O$ (VWR chemicals, Leicestershire, UK)

161   was used as a forming-reagent at a concentration of 1% Ca (w/v). 1H,1H,2H,2H-

162   perfluorohexanol (4:2 FTOH), 1H,1H,2H,2H-perfluorodecanol (8:2 FTOH) and

163   1H,1H,2H,2H-perfluorododecanol (10:2 FTOH) were obtained from Flurochem Ltd

164   (Hadfield, UK) while perfluorooctanoic acid (PFOA), perfluorodecanoic acid (PFDA),

165   perfluorohexanoic   acid   (PFHxA),   perfluoroheptanoic   acid   (PFHpA),

166   perfluorohexanesulfonic acid (PFHxS) and potassium PFOS were obtained from

167   Sigma Aldrich (St Louis Mo, USA). PFAS solutions were prepared in methanol

168   (MeOH,Merck, Darmstadt, Germany) and then diluted with ultrapure water. 99.998%

169   purity argon gas was provided by BOC (Dublin, Ireland). For sample preparation,

170   98% formic acid was used (Fisher Scientific, Loughborough, UK), methyl tert-butyl

171   ether (MTBE) (Merck), ammonium hydroxide (Merck), For coating the graphite

172   furnace Pd, Pt, W (Merck) and Zr (VWR, Leicestershire, England) standard solutions

173   were used. Mg $(NO_3)_2$ (Merck) was used mixed with $Pd(NO_3)_2$ as a chemical modifier

174   in solution.

175   *2.3 Samples*

176   All optimisations were performed with 1:1 MeOH/ H_2O standard of PFOA,

177   PFOS, PFHxS, FTOH 10:2, FTOH 8:2 and FTOH 4:2 at a concentration of 5 mg F L^{-1}.

178

179   The developed method was applied to river water (River Don, Aberdeen,

180   Scotland), sea water (Aberdeen Bay), wastewater and effluent samples (from Nigg

181   WWTW in Aberdeen, Scotland). The sample preparation for the aqueous standards

182   for the calibration curve and the samples, except waste water was performed

183   according to Zacs et al. [32]. Around 200 mL of the centrifuged sample (3000 rpm for

184   5 minutes) where weighed and spiked with 0, 1 and 2 ng fluorine each as PFOA,

185   PFOS, PFHxS, PFHpA, PFDA and PFHxA respectively and 100 µL formic acid.

186   For the wastewater samples, around 10 g (w/w) of sample was spiked with 0, 1

187   and 2 ng fluorine each as PFOA, PFOS, PFHxS, PFHpA, PFDA and PFHxA and left

188   to equilibrate for at least 30 minutes. 5 mL of MeOH and 1 mL of 0.2 mol L^{-1} NaOH

189   were then added. The samples were vortex-mixed and submitted to a 30 minutes

190   ultrasound bath before subsequent centrifugation at 3000 rpm for 10 minutes. The

191   supernatant was then transferred to a 50 mL PP falcon flask and 50 µL of formic acid

192   was added.

193   The samples were added to Oasis weak anion exchange cartridges (Waters

194   Technologies, US), previously conditioned with 3 mL of 30% NH_4OH, 3 mL of

195   MTBE/MeOH (90:10 v/v), 3 mL of MeOH and 3 mL of deionized water. After loading

196   the samples, the cartridges were washed with 1 mL of 2% formic acid and 2 mL of

197 MeOH. After drying for 30 minutes under vacuum, the cartridges were eluted with 7

198 mL of MTBE. The eluates were dried under a stream of nitrogen at 40 ^{o}C and

199 reconstituted with 200 µL of MeOH. In order to fit in the working range, the samples

200 were diluted 100 times just before the quantification. The analysis were carried out

201 in a W-coated graphite furnace platform and submitted to the temperature program

202 according to the Table 1.

203 **Table 1.** Temperature program for F determination via CaF in a W-coated

204 graphite furnace platform. Gas flow MAX in all steps except vaporization step.

Step	Temperature / ^{o}C	Ramp / ^{o}C s^{-1}	Hold / S
Dry 1	70	6	15
Dry 2	70	0	5
Pyrolysis	700	300	10
Vaporization	1900	3000	5
Clean	2100	1000	5

205

206 *2.4 Graphite furnace platform coating*

207 For atomic absorption spectrometry, the permanent modifiers are classified

208 in two groups: platinum group modifier (PGM) and carbide former modifier (CFM),

209 presenting different mechanisms of action with the analyte. Since the thermal

210 behaviour of the diatomic molecules and the interaction with permanent modifiers at

211 high temperatures remains unknown, four permanent modifiers, two from PGM (Pd

212 and Pt) and two from CFM (Zr and W) and a mixture of Pd/Mg nitrates as chemical

213 modifier in solution were chosen for this study. 400 µg of Pd, Pt, Zr or W were used

214 for the permanent graphite platform recoating and a temperature program

215 optimisation was performed by the multivariated study of drying temperature and the

216 univariated study of pyrolysis and vaporization temperature. For platform recoating,

217 ten injections of 40 µL of a 1 g L^{-1} solution of each permanent modifier were used.

218 After each injection, the temperature program described in Table 2 was performed.

219 **Table 2**. Temperature program for Pd, Pt, W or Zr coating. Gas flow MAX in

220 all steps.

Step	T / ^{o}C	Ramp / ^{o}C s^{-1}	Hold / s
1	90	5	40
2	110	1	40
3	130	1	40
4	1200	300	25
5	2100	500	10
6	2100	0	5

221

222 **3. Results and Discussion**

223 *3.1 Per- and polyfluoroalkyl substances*

224 In order to characterise the different behaviour of different common classes of

225 PFASs containing ionic and neutral compound with different volatility and water

226 solubility (Table 2), six different PFASs were chosen: PFOA, PFOS, PFHxS, and 3

227 FTOHs (10:2, 8:2 and 4:2; Figure 1).
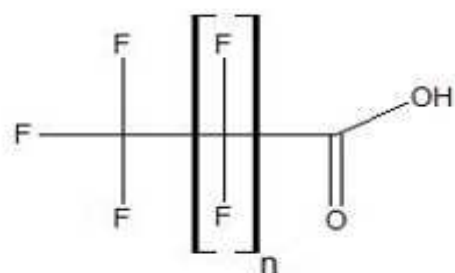
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Perfluoroalkyl carboxylic acids (PFCAs)

n=2: PFBA
n=3: PFPeA
n=4: PFHxA
n=5: PFHpA
n=6: PFOA
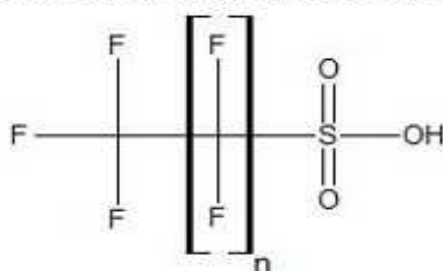
Perfluoroalkyl Sulfonic Acids (PFSAs)

n=5: PFHxS
n=7: PFOS

Fluorotelomer Alcohols (FTOHs)
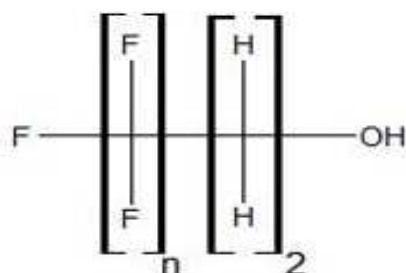
n=4: 4:2 FTOH
n=6: 6:2 FTOH
n=8: 8:2 FTOH
n=10: 10:2 FTOH

Figure 1. Chemical structures of a selection of per- and polyfluoroalkyl substances.

These compounds are distinguished by different functional groups. While PFCA are carboxylic acid and negatively charged in natural waters, PFOS and PFHxS are also negatively charged sulphonic acids. FTOHs are alcohols with different numbers of fluorine-substituted carbons and neutral. Alongside the different physicochemical features such as volatility and solubility, these structural and

253 functional differences could cause different interactions with the graphite surface and

254 modifiers, resulting in different sensitivities and a loss of accuracy, since the

255 inorganic fluoride calibration standard might not behave in the same way as the

256 mixture of PFASs present in the matrix. Since it is not possible to optimise a method

257 for all the known PFASs, these analytes were chosen to be investigated as

258 representatives of compounds with their respective functional groups.

259 **Table 3.** Physicochemical properties of the studied PFASs.

Compound	Molar weight (g/mol)	Solubility in water at 25 ^{o}C (g/L)	Melting point (^{o}C)	Boiling point (^{o}C)
4:2 FTOH	264.09	0.97 [b] [33]	-58 [34]	140-143 [34]
8:2 FTOH	464.12	0.194×10^{-3} [35]	46-50 [33]	112-114 [35]
10:2 FTOH	564.13	$8,9 \times 10^{-4}$ [b] [36]	90-95 [37]	110-145 [37]
PFOA [38]	414.1	9.5	40 - 50	189 -192
PFOS[a] [38]	538[a]	0.68[a]	>400[a]	NDA
PFHxS	400.11	6.2×10^{-3} [39]	NDA	238-239 [40]

260 a: K salt. b: at 22 ^{o}C NDA: No data available.

261 *3.2 Temperature program*

262 As showed in the Table 3, the volatility of the FTOHs is significantly higher

263 than the other PFASs. This can cause loss of the analyte during drying and pyrolysis

264 in the graphite tube. To overcome this issue, a Doehlert multivariate experimental

265 design was performed for each drying step and the temperature and hold time for

266 4:2, 8:2 and 10:2 FTOH were optimised. For this experiment, 5 µL of a 5 mg F L^{-1}

267 solution of each FTOH and 5 µL of a 1% (w/v) Ca aqueous solution were used. The

268 experimental matrix is shown in Table 4.

269

270   **Table 4**. Doehlert experimental design matrix for optimisation of drying step for

271   FTOHs.

Experiment	Drying 1 hold time (s)	Drying 1 temperature (^{o}C)
1	7	70
2	13	70
3	15	80
4	13	90
5	7	90
6	5	80
7 (c)	10	80
7 (c)	10	80
7 (c)	10	80
Experiment	Drying 2 Hold time (s)	Drying 2 temperature (^{o}C)
1	7	70
2	13	70
3	15	80
4	13	90
5	7	90
6	5	80
7(c)	10	80
7(c)	10	80
7(c)	10	80

Figure 2. Response surface for a Doehlert experimental design. For the drying 1 step: a) 4:2 FTOH b) 8:2 FTOH c) 10:2 FTOH. For the drying 2 step: d) 4:2 FTOH e) 8:2 FTOH f) 10:2 FTOH. All experiments were performed with a total of 25 ng of F, T_{pyr}: 900 ^{o}C, T_{vap}: 2000 ^{o}C in a W-coated graphite tube.

277

278   According to the results shown in Figure 2a, for the drying 1 step, the

279   temperature had less influence on the most volatile compound 4:2 FTOH (flat curve

280   and low sensitivity), and was more critical for 8:2 and 10:2 FTOH, which shows a

281   significant increase in instrumental response at lower temperatures (Fig. 2b and c).

282   The fact that this parameter was not significant for 4:2 FTOH may be interpreted as a

283   non-ideal range of study for this compound due to its high volatility, but lower

284   temperatures were not able to satisfactorily dry the solvent. In this study, a longer

285   hold time in a lower temperature produced a more intense signal, with an efficient

286   dry without boiling, which causes loss of analyte by spilt in the windows/wall of the

287   graphite furnace. Also, the lower temperatures avoid losses by volatilization. The

288   same was observed for all analytes and for this reason, the drying 1 temperature

289   was fixed at 70 ^{o}C and held for 15 seconds.

290   About the Drying 2 step, the different temperatures and hold times did not

291   show any improvement for 4:2 FTOH (Fig. 2d), again, probably caused by a non-

292   ideal range of study. For 8:2 FTOH and 10:2 FTOH (Fig. 2e and f), the losses were

293   avoided with a low temperature with a short hold time. By the visual observation of

294   the sample during the drying 2 step, it was possible to ensure the short hold time

295   was enough for a completely dry. For this step, the optimal conditions were fixed at

296   70°C and 5 seconds.

297   The pyrolysis and vaporization steps were univariately optimised for all the

298   studied compounds. 5 µL of a 5 mg F L^{-1} solution from each compound and 5 µL of a

299   1% (m/v) Ca aqueous solution were used in this experiment. The thermal behaviours

300   of F^{-}, PFOA, PFOS, PFHxS, 10:2 FTOH, 8:2 FTOH and 4:2 FTOH were investigated

301 using four different permanent modifiers – Pd, Pt, W and Zr with and without the

302 chemical modifier, Pd/Mg, in solution, and without any kind of modifier (Fig. 3).

303
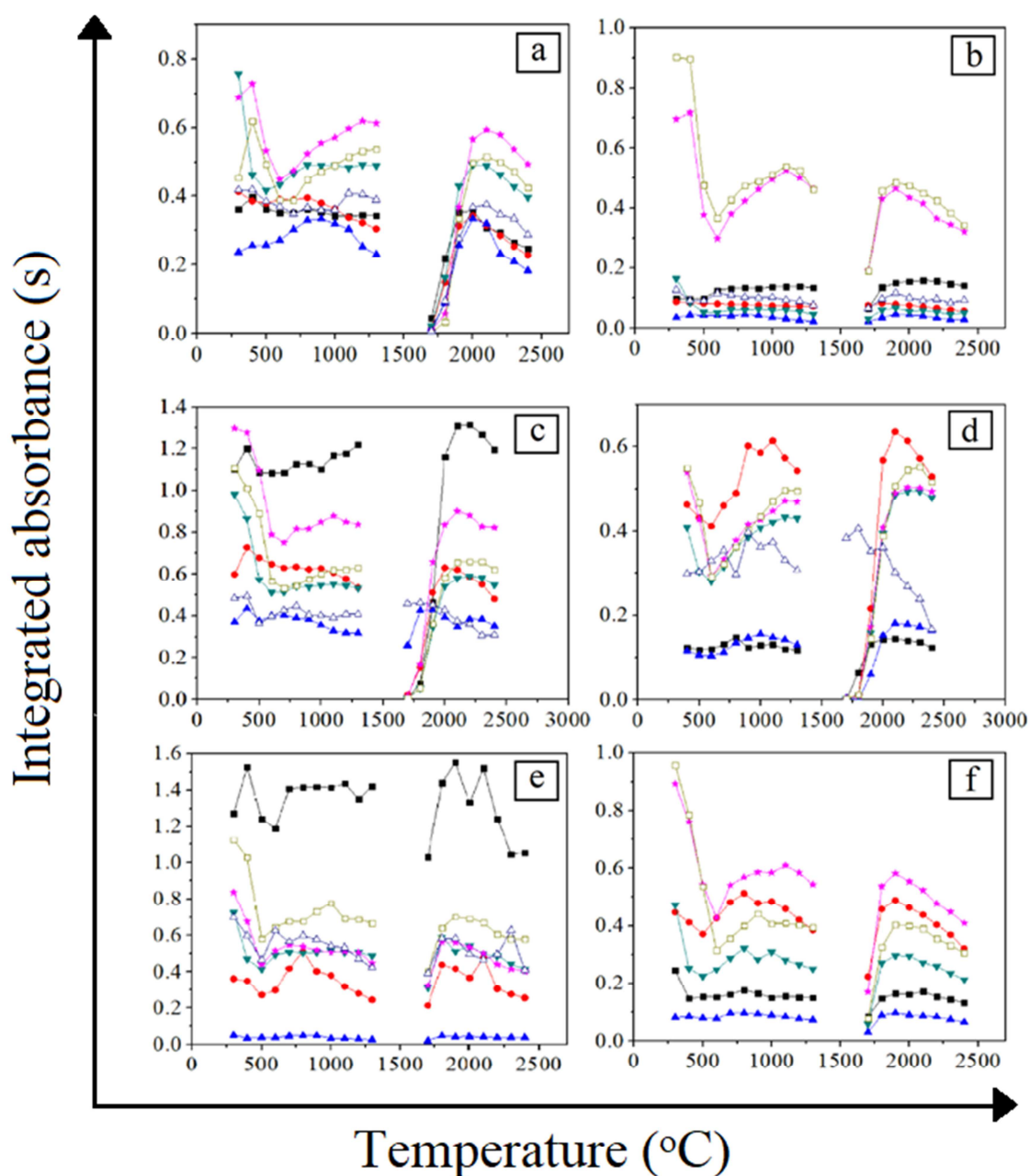
Figure 3. Optimisation of temperature program for aqueous standards of (■)
fluoride; (△)10:2 FTOH; (●) 8:2 FTOH; (▲) 4:2 FTOH; (▼) PFOA; (□) PFHxS and
(★) PFOS performed with 25 ng of F and a) 400 µg of Zr as permanent modifier; b)
400 µg of Pd as permanent modifier + 7.5 ng/ 5 µg of the mixture of Pd/Mg nitrates in

308   solution; c) 400 µg of W as permanent modifier; d) without any permanent modifier;

309   e) 400 µg of Pt as permanent modifier and f) 400 µg of Pd as permanent modifier.

310   For all pyrolysis optimisations T_{vap}: 2000 ^{o}C and for vaporization optimisations T_{pyr}:

311   900 ^{o}C.

312   The main concern regarding determination of total fluorine in an extract is the

313   variation in sensitivity among individual PFASs especially if the fluorine speciation in

314   the extract is unknown. This can lead to inaccurate results as the calibration with

315   fluoride may not be representative of all compounds. As observed in Figure 3, the

316   studied compounds showed not only different thermal behaviours, but their

317   behaviours also varied when different modifiers were used. For the tube without a

318   permanent modifier (Fig. 3d), 4:2 FTOH and fluoride gave the same intensity, but

319   around five times lower than the other analytes. For the Zr-coated graphite tube (Fig.

320   3a), all tested PFASs and fluoride had a similar intensity when a pyrolysis

321   temperature of 700 ^{o}C and vaporization temperature of 1900 ^{o}C were used. This

322   indicates that the permanent modifier Zr is necessary to stabilize fluorine especially

323   from the volatile species. When Pd/Mg was used as a chemical modifier in solution

324   (Fig 3b), most of the substances presented similar and low sensitivity (excepting

325   PFOS and 10:2 FTOH) with the lowest being 4:2 FTOH and fluoride. For the W-

326   coated graphite tube (Fig 3c), the intensity of fluoride was higher than the other

327   analytes but 4:2 FTOH gave the lowest analytical response. PFOS, PFOA and

328   PFHxS behaved similarly, indicating that the perfluorocarboxylic acids (PFCAs) may

329   have a similar mechanism of interaction with this modifier. They might bind with the

330   carboxylic group rather than the fluorine present in these molecules. Despite the

331   disparate thermal behaviours, when the temperature of the vaporization step was set

332   at 1900 ^{o}C, it was possible to obtain similar intensity for all compounds. However, it

333   was not possible to associate the higher intensity with the same analytical response

334   for all compounds. In such cases, a compromise condition was selected as the

335   optimal conditions for non-specific analysis of fluorine in order to obtain the most

336   similar sensitivity among all PFASs and fluoride. Unfortunately, the low analytical

337   response obtained for 4:2 FTOH and 8:2 FTOH in comparison to the other analytes

338   (even with an optimised temperature program) could not be resolved. This is most

339   likely due to the very volatile nature of these compounds. Thus, these two

340   compounds were excluded from further studies and the method considered

341   unsuitable for short-chain FTOHs and most likely to other neutral and volatile

342   PFASs. Two distinct conditions were set for further sensitivity studies: 600 ^{o}C and

343   1900 ^{o}C for the pyrolysis and vaporization steps, respectively, in a Zr-coated

344   graphite tube, and 700 ^{o}C and 1900 ^{o}C for the pyrolysis and vaporisation steps

345   respectively in a W-coated graphite tube.

346   *3.3 Ca/F molar ratio*

347   The ratio between the forming-reagent and analyte were studied for each

348   substance (PFOA, PFOS, PFHxS, 10:2 FTOH and F^{-}). Since there is a possibility of

349   the functional groups compete by the forming-reagent with fluorine (eg. the formation

350   of Ca-S or Ca-H), the concentrations of Ca were studied to avoid loss of sensitivity

351   caused by interference. Mass ratios between 0 – 14000 Ca/F were carried out in a

352   400 µg W-coated graphite tube and the optimised temperature program was applied.

353   According to this study, it is necessary to have a large excess of forming-reagent to

354   achieve the highest intensity signal. For all analytes, the increase in sensitivity is

355   more pronounced up to a ratio of 4000, with only a slight increment up to 12000,

356   where a plateau is achieved. Since no decrease in intensity is noticed with higher

357 concentrations and the forming-reagent is not considered hazardous, the ratio of

358 12000 Ca/F was chosen.
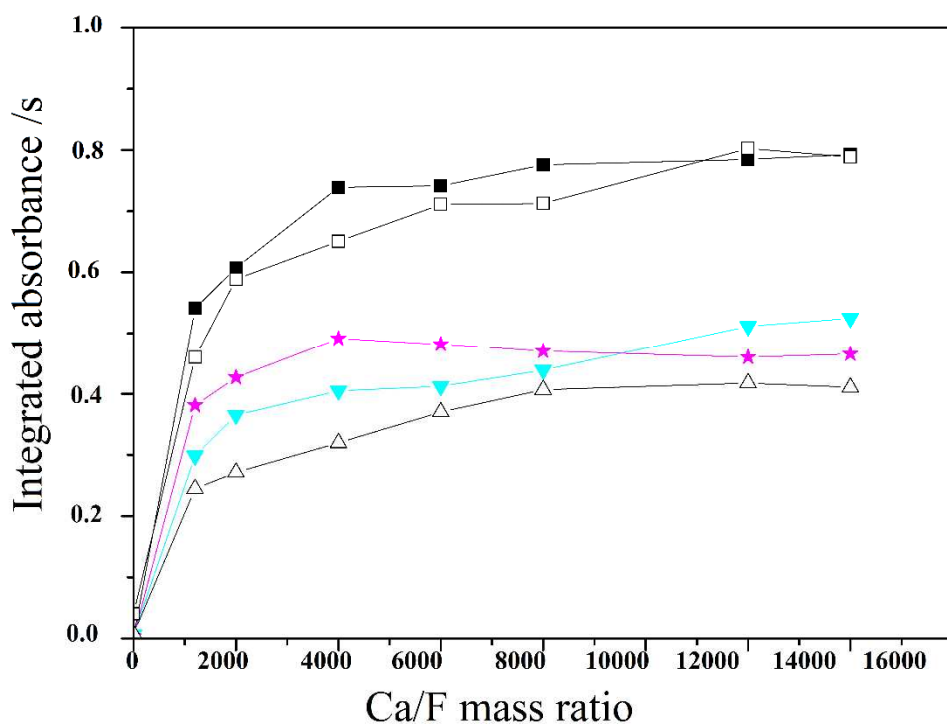
359

360 **Figure 4.** Optimisation of Ca/F ratio for (■) fluoride; (△)10:2 FTOH; (▼) PFOA; (□)

361 PFHxS and (★) PFOS performed with 25 ng of F.

362 *3.4 Sensitivity and calibration curves*

363   PFAS analysis is normally performed in methanolic media (e.g., as EOF),

364 usually following SPE extraction, due to its compatibility with HPLC in reverse phase

365 mode. However, most of the HR-MAS fluorine analyses were carried out with

366 aqueous standards using an inorganic fluoride salt (most commonly KF and NaF)

367 [23–25] Since the PFASs presented unique physical-chemical properties, the

368 sensitivity of these compounds could differ from each other and vary with the solvent

369 used. Furthermore, the solubility of fluoride cannot be guaranteed in every solvent.

370   For this reason, a study of the calibration curve slopes was carried out with each of

371   the selected compounds (PFOA, PFOS, PFHxS, 10:2 FTOH and F$^-$) in aqueous and

372   methanolic solution. The PFASs PFHxA, PFDA and PFHpA in Zr-coated and W-

373   coated graphite tubes were also studied in order to see whether all PFCA behave

374   similar.

375   *3.4.1 Aqueous external calibration*

376   The aqueous calibrations were performed between 1.5 ng – 5 ng (5 µL of 0.3 to 1.0

377   mg L^{-1}), using 50 µg of Ca as the forming reagent, Zr and W as permanent modifiers

378   in the optimised conditions and compared with a method proposed by Mores et al.

379   [28] which also used external aqueous calibration and no permanent modifier. The

380   slope for each PFASs are shown in Table 5.

381   **Table 5.** Aqueous calibration curve slopes obtained using W-coated and Zr-

382   coated graphite tubes with the optimised conditions and calibration curve slopes

383   obtained with the method described by Mores et al. [28]. Average and error are given

384   as standard deviation of triplicates.

	W-coating		Zr-coating		Mores method	
Compound	Slope (mg L^{-1})	R	Slope (mg L^{-1})	R	Slope (mg L^{-1})	R
F$^-$	0.121 ± 0.03	0.998	0.164 ± 0.01	0.996	0.251 ± 0.01	0.997
PFOA	0.116 ± 0.01	0.989	0.104 ± 0.01	0.988	0.115 ± 0.01	0.964
PFOS	0.124 ± 0.01	0.987	0.136 ±0. 01	0.991	0.194 ± 0.03	0.969
PFHxS	0.112 ± 0.01	0.992	0.088 ± 0.01	0.998	0.199 ± 0.03	0.992
10:2 FTOH	0.062 ±0.01	0.987	0.086 ± 0.01	0.963	0.079 ± 0.01	0.992

385

386   A Tukey-Kramer test was applied to evaluate the variance between the three

387   studied methods: Using the optimized conditions presented in this work (for Zr as

388   permanent modifier and W as permanent modifier) and without permanent modifier

389   (according to Mores et al.[28]) and suggested that for a 95% confidence level), the

390   methods did not show a significant difference. However, there is too much noise in

391   the studied data. In this case, an individual analysis of each set of data was needed

392   to evaluate the randomness of the data.

393   When W was used as permanent modifier (Fig. 5-a), a lower variation

394   between the PFASs slopes was achieved when compared with the inorganic

395   aqueous standard. The lowest variation was achieved for PFOS, which was 2%

396   lower compared to fluoride using a W-coated tube, while the higher difference was

397   presented by 10:2 FTOH– 51% when compared with the inorganic fluoride slope.

398   According to a 2-tailed 95% confidence t-test, excepted by 10:2 FTOH, the slopes

399   did not present any significant difference. This means that a calibration with fluoride

400   would be useful for the ionic PFASs with low volatility.

401   The results obtained with the W-coated graphite tube and the optimised

402   conditions can be compared with the method established by Mores et al. [20] for the

403   same analytes (Fig. 5-b). The sensitivities of the different PFASs obtained by this

404   method, using a graphite tube without permanent modifier, pyrolysis temperature of

405   725 ^{o}C and vaporisation temperature of 2250 ^{o}C were completely different. The

406   comparison of the averages varied between 20% for PFHxS and 68% for 10:2 FTOH

407   when the slopes are compared to the average of F^{-} calibration curve. According to a

408   95% confidence 2-tailed t-test, only PFHxS slope was statistically similar with

409   fluoride slope. The method described by Mores et al. [20] seems unsuitable for the

410   determination of extractable organofluorines, being more appropriated the use of W

411   in the optimised conditions, due to the lower difference of sensitivity between the

412   studied compounds.
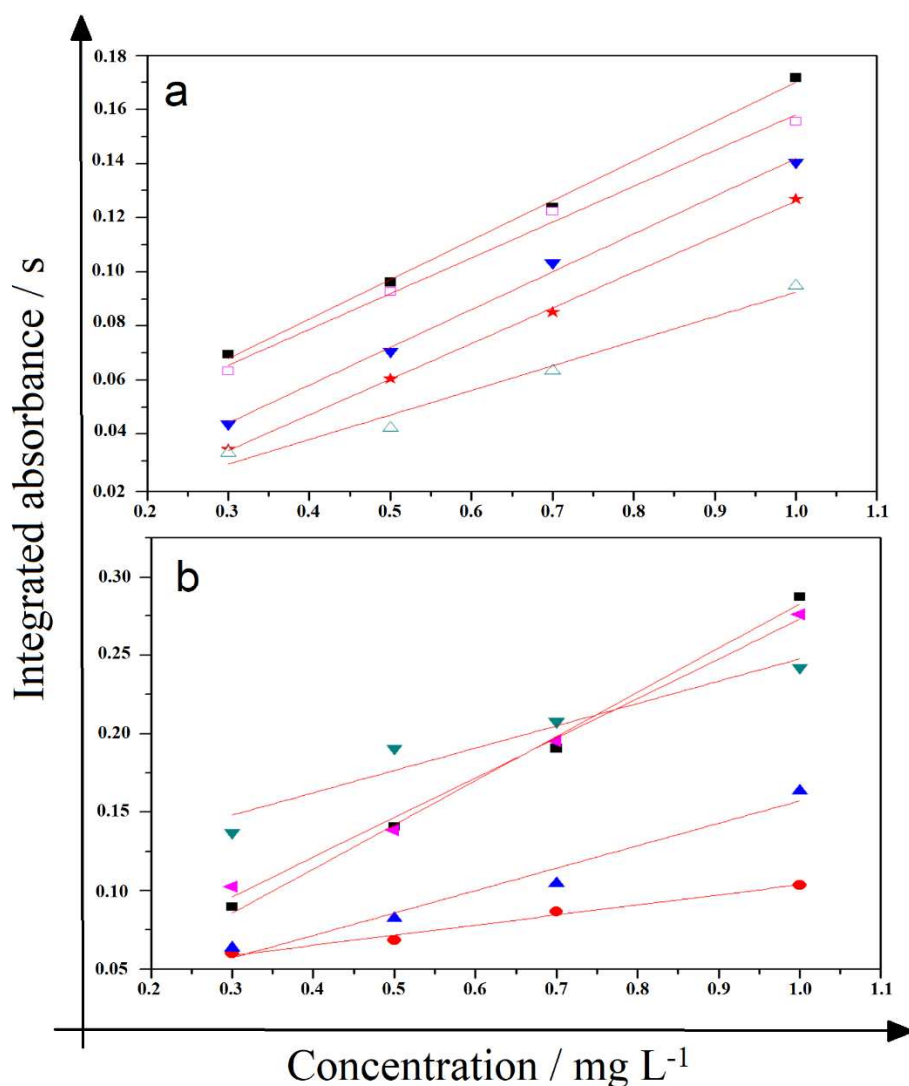
413

414   **Figure 5**. Aqueous standard calibration curve for fluorine from (■) fluoride; (●) 10:2

415   FTOH; (▼) PFOA; (★) PFHxS and (▲) PFOS in a) 400 μg W-coated graphite

416   furnace and optimized conditions (T_{pyr}: 700 °C/ T_{vap}: 1900 °C)(this study) and b)

417   without permanent modifier, according to Mores *et al*. [28] (T_{pyr}: 725 °C/ T_{vap}: 2250

418   °C).

419

420   *3.4.2 Methanolic external calibration*

421   Since the present method was developed to be a tool for mass balance for

422   EOF (extractable organic fluorine), the study of sensitivity was evaluated using

423   methanolic calibration curves, once the methanolic solutions presented a slightly

424   different sensitivity when compared to the aqueous solution. This experiment was

425   performed in the same calibration range, between 1.5 ng – 5 ng F (5 µL of 0.3 to 1.0

426   mg L^{-1}), using 50 µg of Ca as the forming reagent, and Zr and W as permanent

427   modifiers with the optimised temperature conditions. The 10:2 FTOH was not studied

428   in methanolic media because it is not extracted with the chosen sample preparation

429   method. The slopes for both permanent modifiers are shown in Table 6. Since the

430   method described by Mores *et al.* (20) was applied only for aqueous standards and

431   samples, it was not used as comparison for this study.

432   **Table 6.** Methanolic calibration curve slopes obtained with W-coated and Zr-

433   coated graphite tube with the optimised conditions to determine total F in EOF.

434   Average and error are given as standard deviation of triplicates

	W-coating		Zr-coating	
Compound	slope (mg L^{-1})	R	slope (mg L^{-1})	R
F$^-$	0.159 ± 0.02	0.988	0.263 ± 0.02	0.996
PFOA	0.092 ± 0.06	0.999	0.127 ± 0.02	0.986
PFOS	0.099 ± 0.01	0.961	0.106 ± 0.06	0.996
PFHxS	0.101 ± 0.01	0.962	0.128 ± 0.01	0.957
PFHxA	0.098 ± 0.03	0.982	0.125 ± 0.01	0.994
PFHpA	0.098 ± 0.03	0.982	0.085 ± 0.01	0.991
PFDA	0.092 ± 0.03	0.969	0.111 ± 0.02	0.989

435

436   It is obvious that using a methanolic solution fluoride cannot be used as calibrant for

437   the different PFAS both coatings, due to the discrepant sensitivity when compared to

438   the other species. For the calibration performed in a Zr-coated graphite tube, the

439   PFASs slopes presented a relative difference from 52% to 68 % − when compared

440   with the aqueous F⁻ standard. However, the sample preparation aims to the

441   µµdetermination of total fluorine in the extractable organofluorines (EOF), and the

442   concentration of F⁻ is negligible since it would not be extractable in the non-polar

443   solvents. Comparing the averages of the slopes of all compounds with the PFOA

444   calibration curve, the variation of the slopes was between 1% for PFHxS and 32%

445   for PFHpA. The other standards gave slopes between 2% and 17%. According to a

446   95% confidence 2-tailed t-test, with exception of PFHpA, no significant differences

447   were found between PFOA and the other PFASs.

448   For the W-coated graphite tube, the slope variation of the PFASs when compared

449   with F⁻ was also high, from 36% to 50%. However, when the slopes are compared

450   with the PFOA calibration curve, the difference among them was lower than 15%. 2-

451   tailed t-tests with 95% confidence between PFOA slope compared with the other

452   PFASs were evaluated, and no significant difference were found for any of the

453   studied compounds. For this reason, W-coated graphite tube was chosen for the

454   quantification of total fluorine of the EOF.

455   *3.5 Figures of merit and the determination of total organic-F in river, seawater,*

456   *wastewater and effluent samples using SPE sample preparation*

457   A brand new graphite tube was coated with 400 µg W to provide a higher

458   sensitivity and lower standard deviation, since a poorly coated or porous surface can

459   affect negatively the obtained results. The temperature program was set according to

460   the optimised conditions (Table 1). The calibration curve was constructed using

461   PFOA standard solutions with subsequent use of SPE according to the session 1.3

462   of this present work, in a working range of 1.5 ng – 7.5 ng F. The sample volume

463   was fixed to 5 µL of sample to avoid deviations caused by an incomplete dry of

464   higher volumes. It was used 12 µL of a 1% Ca solution as forming reagent. The

465   samples were enriched with a mix of PFOA, PFOS, PFHxS, PFHxA, PFHpA and

466   PFDA. In order to fit in the working range, the samples were diluted in methanol

467   around 100 times just before the analysis and the final concentration were 5 µg L^{-1}

468   and 10 µg L $^{-1}$. The limit of detection and quantification were calculated based on 3

469   and 10 times the standard deviation of 10 measurements of blank divided by the

470   calibration curve slope, respectively. The limit of detection for the method using SPE

471   as sample preparation was 0.3 µg L^{-1} and the limit of quantification was 1 µg L^{-1}. A

472   summary of the figures of merit is shown in Table 7.

473   **Table 7**. Figures of merit for fluorine determination *via* CaF under optimised

474   conditions and SPE methanolic PFOA extract standard external calibration.

Parameter	Value
Equation	y= 0.159x + 0.031
R^2	0.999
LOD $_{inst}$	0.1 mg L^{-1}
LOQ $_{inst}$	0.3 mg L^{-1}
LOD $_{SPE}$	0.3 µg L^{-1}
LOQ $_{SPE}$	1.0 µg L^{-1}
Working range	0.3 mg L^{-1}- 1.5 mg L^{-1}

475   Inst = instrumental parameter SPE = method parameter x = mg L^{-1}

476   The recovery rate for the selected samples (Table 8) was satisfactory, especially

477   when considering the complexity of the matrices. The wastewater samples had the

478   lowest recovery rate (around 72%). However, this complex matrix presented a high

479   level of dissolved solids. It is well known that PFASs are easily adsorbed [40], which

480   could explain the low recovery rate, since only the fluorine present in the supernatant

481   is quantified.

482   **Table 8**. Concentrations and recovery of total F from PFASs enrichment (spike),

483   after extraction by SPE (n=3).

Sample	unspiked matrix (μg F L^{-1})	Percent recovery	
		5 μg F L^{-1}	10 μg F L^{-1}
Sea water	<1.0	103 ± 17%	80 ± 2%
River water	14.5 ± 0.1	112 ± 3%	101 ± 3%
Effluent	<1.0	136 ± 9%	85 ± 1%
Wastewater	<1.0	68 ± 2%	75 ± 2%

484

485   **4. Conclusion**

486   The present paper showed that different organofluorine compounds exhibit

487   different thermal behaviour and sensitivity for HR-GF MAS for total F quantification

488   via CaF. Through an optimisation of temperatures and permanent modifiers, it was

489   possible to achieve similar sensitivities among selected PFASs with different

490   perfluoroalkyl chain lengths and functional groups. However, the developed method

491   proved to be unsuitable for short chain FTOHs, which had extremely low sensitivity

492   when compared to the other PFASs due its high volatility and loss in the drying step.

493   This work introduces a completely new approach to total fluorine determination,

494 since most papers only work with inorganic standards and aqueous media, which is

495 not applicable for the mass balance of organofluorine. The combination of a sample

496 preparation method to preconcentrate the analyte and the optimised temperature

497 program allowed low limits of detection and quantification to be achieved, making it

498 possible to quantify total F in the low ppb range. Although other possible

499 organofluorines such as F-containing pharmaceuticals require further testing, this is

500 a first approach to optimise the modifiers and temperature programmes for PFAS

501 determination in complex environmental samples. The developed method can

502 therefore be used for total fluorine determination in organic extracts or in the often

503 used EOF (extractable organofluorines) when only ionic PFASs such as PFCAs and

504 PFOS occur.

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Highlights:

- Response optimisation for individual PFAS
- Same response for ionic extractable organofluorines using HR-GF-MAS
- Low response for volatile neutral PFAS
- Validation for total fluorine determination of PFCAs in water samples

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: