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# 1 Manuscript for JAAS

## 2 3 Plasma processes to detect fluorine with ICPMS/MS as [M-F]<sup>+</sup>: an 4 argument for building a negative mode ICPMS/MS

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### 11 12 Abstract:

13 Detection of fluorine with commercial ICPMS is impossible due to fluorine's high ionisation  
14 potential (IP). A novel approach through the formation of fluorine-containing polyatomic ions  
15 [M-F]<sup>+</sup> in the plasma allows the successful detection of F in sub ppm level by ICPMS/MS. Two  
16 theories behind [M-F]<sup>+</sup> formation have been proposed, yet there is no clear understanding  
17 about this mechanism. Here, different metal solutions were tested to study the  
18 characterisation of plasma processes in the formation of [M-F]<sup>+</sup>. Three characteristics: high  
19 [M-F]<sup>+</sup> bond dissociation energy (BDE), low [M-O]<sup>+</sup> BDE and low IP, found to be essential to  
20 get highest sensitivity of [M-F]<sup>+</sup>. It was found that for elements with a higher [M-F]<sup>+</sup> BDE than  
21 [M-O]<sup>+</sup> BDE, the sensitivity decreases linearly with the element's second IP, meaning that the  
22 major process in the plasma is that M<sup>2+</sup> harvests F<sup>-</sup> in the plasma to form [M-F]<sup>+</sup>. Barium  
23 exhibited the highest sensitivity for [M-F]<sup>+</sup>. However, the robustness of this approach was  
24 questioned due to matrix effects, hence an argument for re-developing the negative ion  
25 ICPMS/MS was discussed with which detection limits of sub-ppb could be reached.

### 26 27 28 Introduction

29  
30 Inductively coupled plasma mass spectrometry (ICPMS) is well known as a powerful analytical  
31 tool in analysing almost all elements in the periodic table with lower detection limit. Since the  
32 introduction of ICPMS in 1980s and until now this technique has been mainly used in the  
33 positive ion mode. As the ionisation potential (IP) of fluorine is high (17 eV), no significant  
34 amounts of F<sup>+</sup> are generated in the plasma. Therefore, fluorine cannot sensitively detected  
35 directly using a commercial argon plasma ICPMS. Since significant interference from  
36 polyatomic ions form in ICPMS, an attempt has made to use this concept to detect fluorine  
37 by producing [M-F]<sup>+</sup> ions and separate them from other polyatomic ions using ICPMS/MS.

38  
39 Polyatomic ions form from the reaction and collision between ions and/or atoms arising from  
40 elements, which are present abundantly in the plasma, sample and/or solvent. The  
41 temperature is a key factor to determine at which point in the plasma the polyatomic ions are  
42 formed. This is concurrently related to the bond dissociation energy (BDE) of the polyatomic  
43 ions as the weaker BDE ions can be break with the high temperature while high BDE ions stay

1 stable in the plasma. Hence, a metal that has high BDE with fluorine has been chosen by  
 2 Yamada to form poly-nuclear fluorine ions in the plasma.<sup>1</sup>

3  
 4 An attempt has been made to use a barium solution to form significant amounts of [BaF]<sup>+</sup> so  
 5 that detection limits around 0.05 mg/L could be achieved when oxygen or ammonia were  
 6 used as reaction gases in the ICPMS/MS.<sup>2-4</sup> This approach was then applied for total fluorine  
 7 analysis in drinking water and food as well as fluorine speciation analysis.<sup>2-5</sup> Two theories  
 8 exist on how these poly-nuclear ions are generated in an argon plasma. However, the  
 9 mechanism behind these theories remains unclear.



10  
 11  
 12  
 13 In the past, few attempts have been made to detect fluorine with negative-ion ICPMS.<sup>6,7</sup>  
 14 Apparently, detection limits of 0.4 mg/L for fluorine can be achieved in negative ion mode  
 15 with a simple quadrupole instrument capable to switch from positive to negative ion  
 16 detection as it is common for molecular mass spectrometer.<sup>6</sup> Despite the lack of collision or  
 17 reaction cells and the resulting high background, better limit of detection for fluorine and  
 18 chlorine were observed using the negative mode detection than the positive mode. Hence,  
 19 with today's technology of triple quadrupoles and lens configuration, lower background  
 20 coming from polyatomic interference ions, for example [<sup>16</sup>O<sup>1</sup>H<sub>3</sub>]<sup>-</sup> or [<sup>18</sup>O<sup>1</sup>H]<sup>+</sup> can be eliminated  
 21 and better extraction of analyte ions would be expected in negative mode of ICPMS. However,  
 22 these ICPMS instruments are no longer commercially available nowadays, despite their high  
 23 potential in analysing halogens as well as other negative ions. Therefore, in this study a deeper  
 24 understanding about the mechanism of [M-F]<sup>+</sup> was investigated involving the characterization  
 25 of the plasma processes of [M-F]<sup>+</sup> formation. In addition, the implication to improve the  
 26 detection limits and robustness of the fluorine detection using ICPMS/MS was also studied.

## 29 Experimental Section

### 30 Chemicals, standards and reagents

31 Milli-Q water (18 MΩ cm, Smart2Pure, Thermo Fisher Scientific, UK) was used for all analytical  
 32 purposes. Fluorine standards for optimisation and calibration were prepared from potassium  
 33 fluoride (Fisher Scientific, UK) and hydrogen fluoride (Fisher Scientific, UK). Metal standards  
 34 were prepared from Ba(NO<sub>3</sub>)<sub>2</sub> (BDH, UK), Ca (SCP science, Canada), Ce (Sigma-Aldrich,  
 35 Switzerland), Er (Inorganic Ventures, USA), Eu (SCP science, Canada), Gd (SCP science,  
 36 Canada), La (Sigma-Aldrich, Switzerland), Sr(NO<sub>3</sub>)<sub>2</sub> (BDH, UK), Pr (Sigma-Aldrich, Switzerland)  
 37 and Yb (SCP science, Canada).

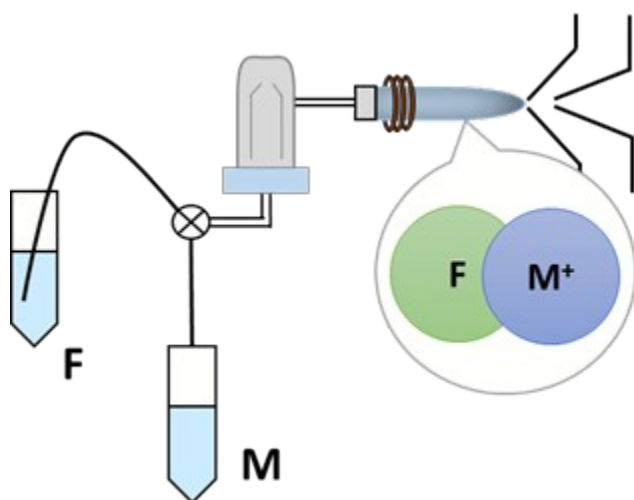
### 39 Instrumental setup:

40 Optimisation and analysis was carried out using an 8800 Triple Quadrupole ICPMS/MS  
 41 instrument (Agilent Technologies, UK) with a micromist nebuliser, nickel sampler and  
 42 skimmer cone and S-lens. As shown in Figure 1, the instrumental set-up for polyatomic ions  
 43 [M-F]<sup>+</sup> analysis followed the previous study.<sup>4</sup> The ICPMS/MS parameters described in Jamari  
 44 et al.<sup>4</sup> were optimised for each metal (M) to get the maximum sensitivity, while for [Ba-F]<sup>+</sup>,

the same parameters as in our previous study were used. The ICPMS/MS was tuned daily for maximum sensitivity and Table 1 shows the details of investigated  $[M-F]^+$  while Table S1 shows the optimum parameters for each metal investigated. The sensitivity of each  $[M-F]^+$  were illustrated as corrected SBR, which was calculated based on the isotopic abundance of the measured isotopes for each metal and corrected for moles (calculation shown in supporting information).

**Table 1:** Investigated fluorine-containing polyatomic ions  $(M-F)^+$  for fluorine detections.

Metal	Ba, Sr, Yb, Ca, Eu, Er, Gd, La, Pr
$m/z$	157 $[Ba-F]^+$ , 107 $[Sr-F]^+$ , 193 $[Yb-F]^+$ , 59 $[Ca-F]^+$ , 172 $[Eu-F]^+$ , 185 $[Er-F]^+$ , 179 $[Gd-F]^+$ , 158 $[La-F]^+$ , 160 $[Pr-F]^+$ , 159 $[Ce-F]^+$
Metal concentration	50 mg/L
F concentration	0.1-10 mg/L



**Figure 1:** Instrumental set-up for fluorine detection using ICPMS/MS. M is the metal containing solution, while F is the fluorine containing solution.

### Results and discussion:

Interferences are the most common problems in ICPMS analysis involving atoms from plasma, solvent and entrained air. Like other ICPMS analysis, metal-fluorides also suffer from isobaric interferences that have the same mass-to-charge ( $m/z$ ) as the analyte. For example, at  $m/z$  157,  $[Ba-F]^+$  have the isobaric interference from barium oxide ions (e.g.,  $[^{138}Ba^{18}O^1H]^+$ ,  $[^{137}Ba^{18}O^2H]^+$ ,  $[^{138}Ba^{16}O^1H_3]^+$ , and  $[^{138}Ba^{17}O^2H]^+$ ). As our previous study revealed that plasma conditions are crucial for the formation of polyatomic ions and reducing the interferences.<sup>4</sup>

Two mechanisms shown in equation 1 and 2 were proposed for the formation of  $[Ba-F]^+$ . Since Ba has low first IP (5.2 eV), mechanism in equation 1 was expected the dominant process occur in the plasma. However, the formation of polyatomic ions  $[Ba-F]^+$  were more efficient in the hot plasma compared to the cool plasma (Figure 2a). This hot environment could

1 promote the formation of the doubly charged ions,  $Ba^{2+}$  since Ba has a low second IP (10.0 eV). Apart from that, the highest intensity of  $[Ba-F]^+$  was mainly deep in the plasma with low sampling position (7.5-8.5 mm). The maximum signal-to-background ratio (SBR) of  $[Ba-F]^+$  also did not coincide with the maximum intensities of either  $Ba^+$  or  $Ba^{2+}$  (Figure 2b). The location in the plasma for the highest intensity of  $[Ba-F]^+$  did not coincide with the location where barium showed the highest intensities for both  $Ba^+$  and  $Ba^{2+}$  respectively. This means that the formation  $[Ba-F]^+$  is limited by F (either  $F^0$  or  $F^-$ ) rather than amount and type of barium ion in the plasma.

10 In order to identify whether the amount of barium would change the location of the highest intensity of  $[Ba-F]^+$ , the amount of added Ba was varied and the sampling location varied. As shown in Figure 3, the place of the highest sensitivity of  $[Ba-F]^+$  was independent on the Ba concentration. The sensitivity of  $[Ba-F]^+$  increase with an increase of the added Ba concentrations between 10-100 mg/L. However, the counts barely increase from 50 to 100 mg/L. hence it is reasonable to use 50 mg/L to avoid clogging of the sampler and skimmer cone with too high concentrations of barium (Figure S2). When there is excess metal present in the plasma,  $[M-F]^+$  can be detected. Since Ba is present abundantly in the plasma, this suggests that instead of Ba species, F plays a role in limiting the formation of  $[Ba-F]^+$  polyatomic ion. Due to the fact that F cannot be measured directly by ICPMS/MS, the influence of thermochemical properties were studied to gain better understanding which mechanism involved in the formation of  $[BaF]^+$  polyatomic ions is the predominant one.

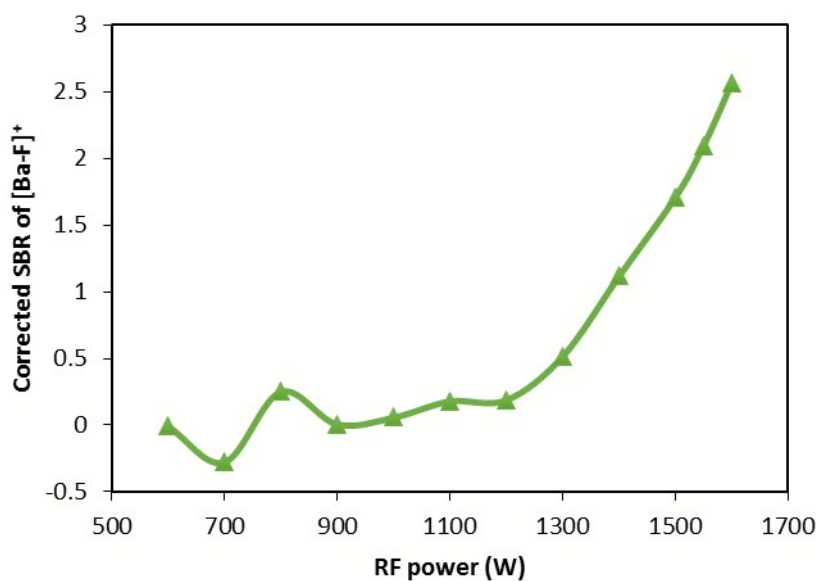
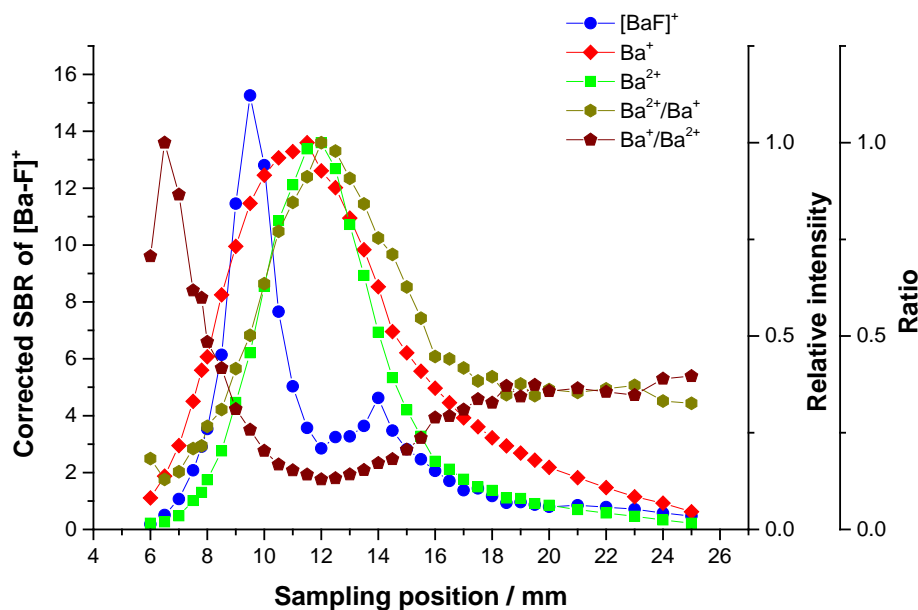
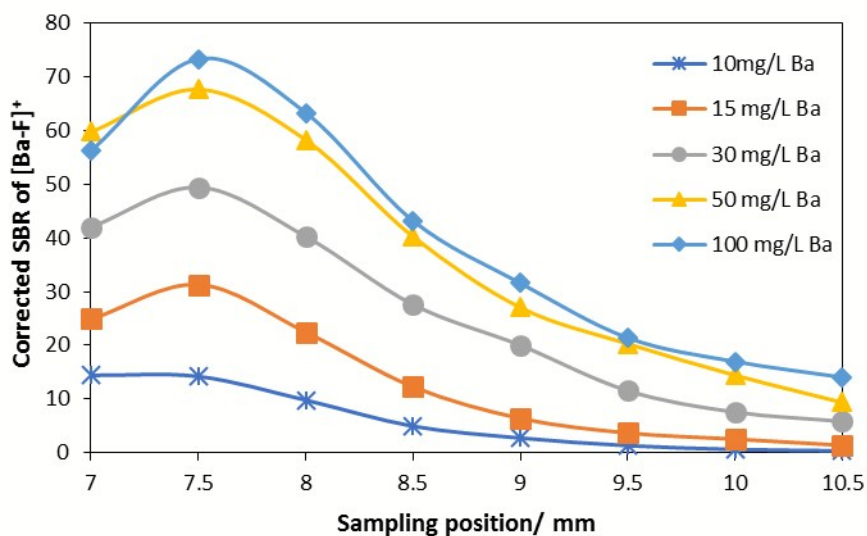


Figure 2a: The sensitivity of  $Ba-F^+$  at different RF powers.



**Figure 2b:** The SBR of  $[\text{Ba-F}]^+$ , relative intensities of  $\text{Ba}^+$  and  $\text{Ba}^{2+}$ , and intensity ratios on different sampling position. The  $[\text{Ba-F}]^+$  signal is illustrated on left Y-axis, relative intensities and intensity ratio of  $\text{Ba}^+$  and  $\text{Ba}^{2+}$  on the right Y-axis.



**Figure 3:** The normalized sensitivity of  $[\text{Ba-F}]^+$  on different Ba concentration recorded at different sampling position.

As has been described by Yamada,<sup>1</sup> thermochemical properties of metals such as BDE and IP are the key factors for an efficient formation of the  $[\text{M-F}]^+$  polyatomic ions. Since oxygen is present abundantly in the plasma, the BDE between fluorine and oxygen-containing polyatomic ions needs to be considered as well. Ba has a high affinity to F (high BDE for  $[\text{Ba-F}]^+$  of 6.39 eV), a low affinity to O (low BDE for  $[\text{Ba-O}]^+$  of 4.00 eV) and a low first and second IP was expected to be the best candidate for an efficient  $[\text{M-F}]^+$  formation. Due to the given working hypothesis that the stability of  $[\text{M-F}]^+$  is essential to achieve the highest sensitivity for a fluorine containing polyatomic ion, a series of metal solutions were used to investigate



1 this hypothesis. Table 2 and Figure S1 illustrate the BDE and IP of different metals (M) from  
 2 alkaline earth and lanthanoid groups.

3  
 4 Figure 4a displays the sensitivity of each  $[M-F]^+$  versus the BDE of metals-fluoride ion. All  
 5 metals have similar BDE with fluorine, but only Ba, Sr and Eu exhibited a significant SBR as  $[M-$   
 6  $F]^+$ , whereas very low or negative SBRs were recorded by other metals. These data  
 7 demonstrate that a strong  $[M-F]^+$  bond alone was not sufficient to explain the formation and  
 8 detection of  $[M-F]^+$  solely. As the SBR is highly depending on the ratio between the  $[M-F]^+$  and  
 9 the  $[M-OH]^+$  species in the plasma, it is necessary to observe the influence of the  $[M-O]^+$  bond  
 10 as well. Figure 4b shows the SBRs of various  $[M-F]^+$  versus the differences of BDEs between  
 11  $[M-F]^+$  and  $[M-O]^+$ . The metals with a stronger BDE for  $[M-O]^+$  than  $[M-F]^+$  bond are illustrated  
 12 as red triangle resulted in high amounts of interfering metal oxides ions in the plasma; hence  
 13 low SBR. Yet, this does not explain the low sensitivity of Yb and Ca. Although both have  
 14 stronger BDE for  $[M-F]^+$  than  $[M-O]^+$ , they exhibited lower sensitivity compared to Ba, Sr and  
 15 Eu. Hence, the BDE differences between the fluorine and the oxide ions would not explain the  
 16 formation and detection of the  $[M-F]^+$  solely.

17  
 18 **Table 2:** The IP and DBE of fluorine and oxygen for different metals.

Metal	1 <sup>st</sup> IP (eV)	2 <sup>nd</sup> IP (eV)	BDE $[M-F]^+$ (eV)	BDE $[M-O]^+$ (eV)	References
<b>Be</b>	9.32	18.2	6.21	4.05	
<b>Mg</b>	7.65	15.0	4.26	2.26	
<b>Ca</b>	6.11	11.9	5.42	3.12	8–10
<b>Sr</b>	5.70	11.0	5.43	3.06	
<b>Ba</b>	5.21	10.0	6.39	4.00	
<b>La</b>	5.58	11.1	6.83	8.73	
<b>Ce</b>	5.54	10.8	6.35	8.80	
<b>Pr</b>	5.46	10.5	6.34	8.23	
<b>Nd</b>	5.53	10.7	6.24 ± 0.21	7.76	
<b>Sm</b>	5.64	11.7	6.29 ± 0.16	5.80	
<b>Eu</b>	5.67	11.2	6.05 ± 0.16	4.00	
<b>Gd</b>	6.15	12.1	6.10 ± 0.25	7.47	11,12
<b>Tb</b>	5.86	11.5	6.43	7.33	
<b>Dy</b>	5.94	11.7	5.54 ± 0.25	6.11	
<b>Ho</b>	6.02	11.8	5.33 ± 0.21	6.24	
<b>Er</b>	6.10	11.9	5.69 ± 0.25	5.96	
<b>Tm</b>	6.20	12.0	5.57 ± 0.16	4.92	
<b>Yb</b>	6.25	12.2	5.78 ± 0.15	3.87	
<b>Lu</b>	5.43	13.9	3.91	5.34	

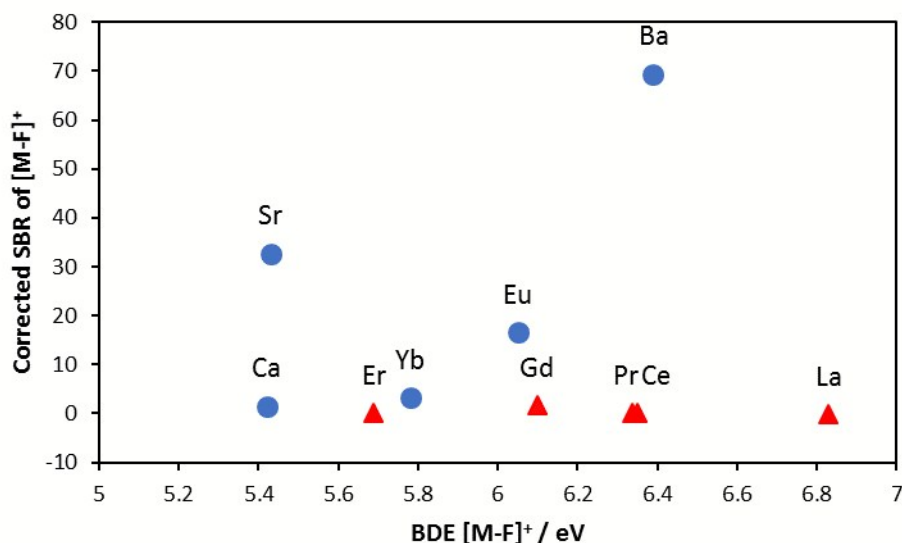


Figure 4a: Corrected SBR of [M-F]<sup>+</sup> dependent on BDE of metal with fluorine [M-F]<sup>+</sup>.

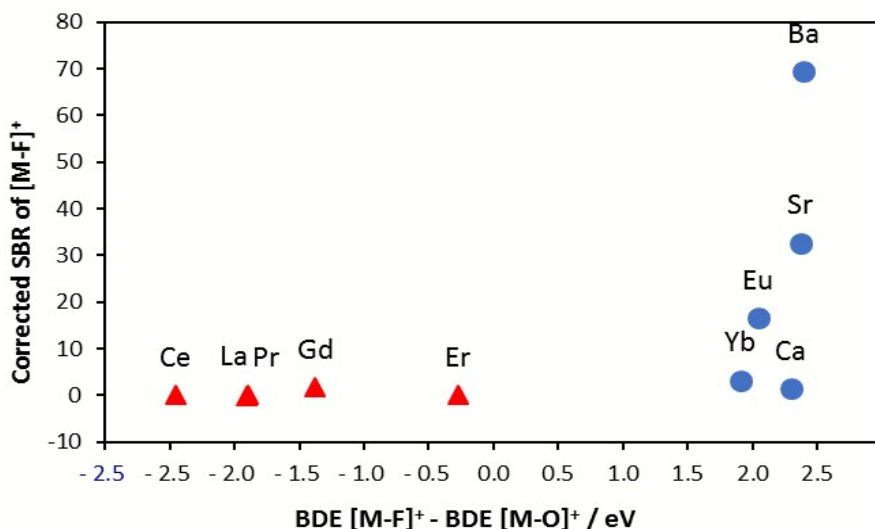


Figure 4b: Corrected SBR of [M-F]<sup>+</sup> based on the difference between BDE of [M-F]<sup>+</sup> and [M-O]<sup>+</sup>. Positive BDE differences illustrated as circle (blue) while negative BDE differences illustrated as triangle (red).

To find an explanation why Ba, Sr and Eu showed significant SBRs although their [M-F]<sup>+</sup> bond is comparable with others; another thermodynamic parameter was studied. The first and the second IPs of each metals were investigated to explain the sensitivity of [M-F]<sup>+</sup>. Based on Figure 5a and 5b, metals with good sensitivity (Ba, Sr and Eu) have lower first and second IPs compared to Ca and Yb, although all of them have positive BDE differences between [M-F]<sup>+</sup> and [M-O]<sup>+</sup>. Meanwhile, metals with negative BDE differences (illustrated as red triangle) have low SBR despite their lower first and second IPs; especially Ce, Pr and La. A correlation study also reveals that there is significant relationship between sensitivity and low IPs (p-value < 0.05) (Table 3). This result discloses that both BDE and IP are essential in the formation of [M-F]<sup>+</sup> and as shown in Figure 5b, Ba with the lowest IPs exhibit the highest sensitivity. Hence, high affinity of Ba with fluorine, low affinity of Ba with oxygen and low IPs



1 making Ba as the most promising metal for an efficient formation of [M-F]<sup>+</sup> with the highest  
 2 sensitivity which is in accordance with the working hypothesis.

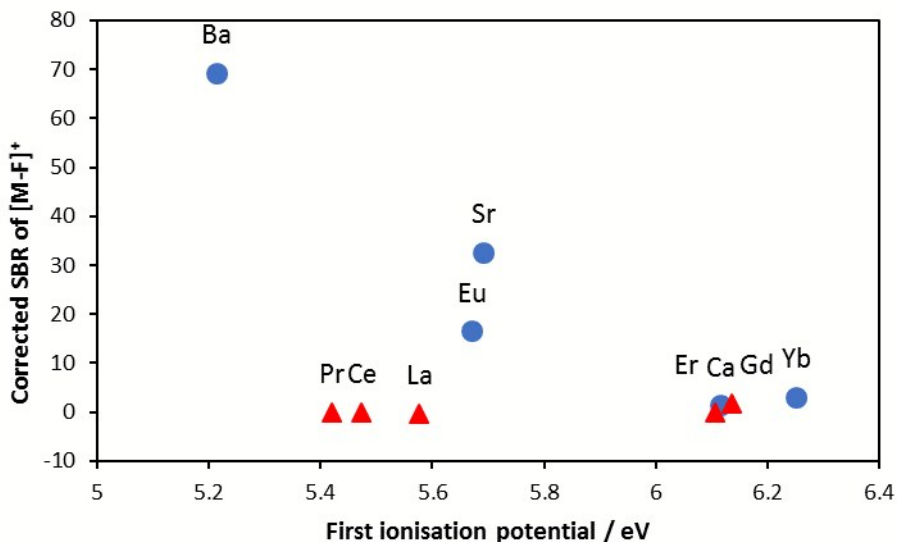
3  
 4 The elemental behaviour of [M-F]<sup>+</sup> formation and detection in relation to the first and the  
 5 second IPs suggest that the second IP is more important than the first IP for the formation of  
 6 [M-F]<sup>+</sup>. This is well illustrated by Eu and Sr. Although Eu has a marginally lower first IP (5.67  
 7 eV) than Sr (5.70 eV), the sensitivity of Eu is lower. The stronger linear increase in sensitivity  
 8 of [M-F]<sup>+</sup> with decreasing second IP illustrates well (Table 3), that the formation of [M-F]<sup>+</sup>  
 9 depends on the occurrence of M<sup>2+</sup> rather than M<sup>+</sup>. As shown in Figure S3a and S3b, the similar  
 10 results exhibited when the SBR was adjusted based on the molarity of the measured isotope.  
 11 These findings indicate that the predominant occurring in the plasma is that M<sup>2+</sup> binds with F<sup>-</sup>  
 12 to form [M-F]<sup>+</sup>.

13  
 14 From our experiences, it has been noticeable that the formation of [M-F]<sup>+</sup> is notorious  
 15 unstable (Figure S4) and highly matrix dependent when easy to ionise metals were added to  
 16 the plasma (Figure S5 and S6). No major effect was observed in the presence of methanol,  
 17 chloride and sulphate indicating that the carbon enhancement effect is not influencing the  
 18 formation and detection of [Ba-F]<sup>+</sup> (Figure S7). However, as shown in Figure 6 by the  
 19 calibration graph, fluoride solutions containing easily ionisable elements show signal  
 20 enhancement of [Ba-F]<sup>+</sup>. This can be explained by the low first IP of potassium (4.3 eV) and  
 21 sodium (5.1 eV). Both elements, added in excess to the F concentration increase the electron  
 22 density and therefore may increase the plasma temperature.<sup>13</sup> Fluorine has high electron  
 23 affinity, the excess of electrons might forces the equilibrium towards F<sup>-</sup> (equation 3). The  
 24 higher plasma temperature may also influence the [M-F]<sup>+</sup> formation. Since potassium has a  
 25 lower first IP compared to sodium, higher electron density was expected to be produced in  
 26 the plasma from the fluoride solution containing potassium. This was however not the case  
 27 indicating another process in the plasma is significant for the [Ba-F]<sup>+</sup> formation and detection.  
 28 The higher electron density might also force the equilibrium of Ba<sup>2+</sup> towards Ba<sup>+</sup>, thus reduce  
 29 the sensitivity of [Ba-F]<sup>+</sup> (equation 4).

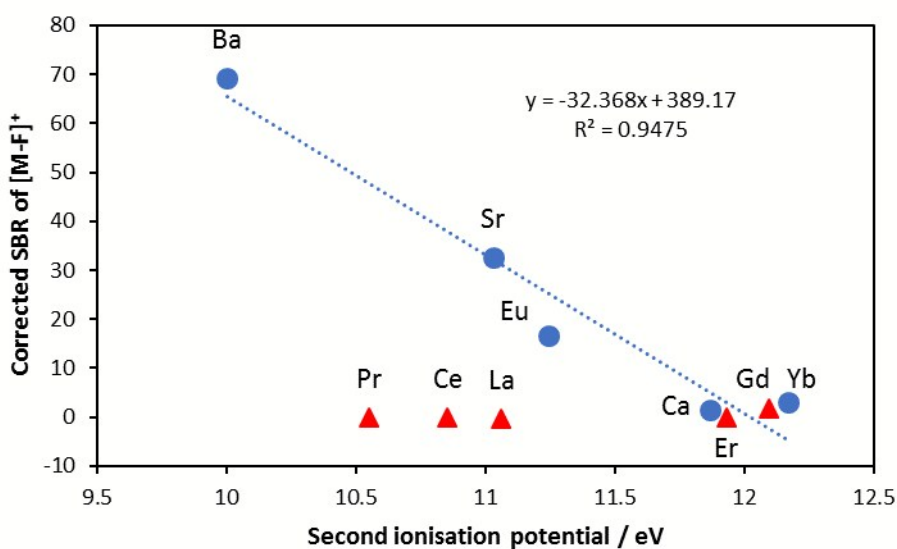


32  
 33  
 34 In comparison with Sr and Eu, the calibration graphs with fluoride solution containing  
 35 potassium and sodium did not really affect the sensitivity of [M-F]<sup>+</sup> (Figure S6 and S7). This  
 36 can be explained by the higher second IP of both Sr and Eu compared to Ba, restraining the  
 37 production of M<sup>2+</sup> in the presence of high electron density. Based on these findings, it can be  
 38 concluded that the predominant process occurring in the plasma is that M<sup>2+</sup> binds with F<sup>-</sup> to  
 39 form [M-F]<sup>+</sup>.

40  
 41 Since F<sup>-</sup> abundance is most important, it would be useful to sample directly this ion and detect  
 42 F<sup>-</sup> direct by the use of a negative mode ICPMS. This has been done in the past with ICPMS  
 43 designed in the late 1980s by the Hieftje group.<sup>6,14</sup>



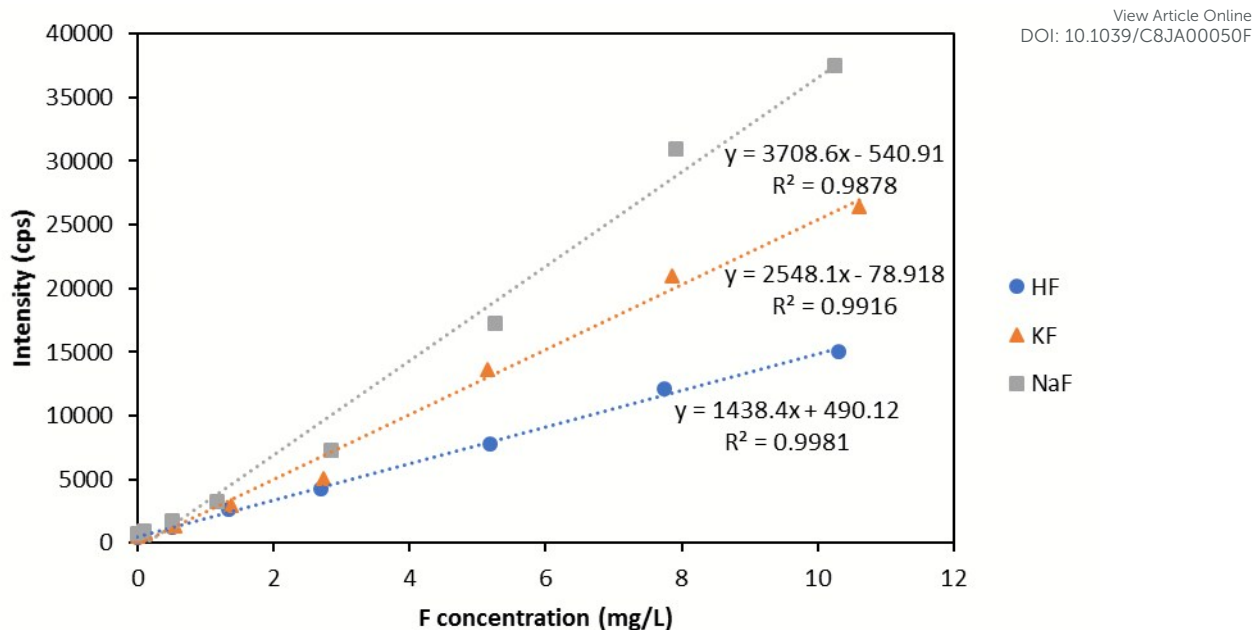
**Figure 5a:** Corrected SBR of  $[M-F]^+$  dependent on the first IP of metals ( $M$  to  $M^+$ ). The symbols description same as displayed in Figure 3b.



**Figure 5b:** Optimised SBR of  $[M-F]^+$  dependent on the second IP of metals ( $M^+$  to  $M^{2+}$ ). The symbols description same as displayed in Figure 3b.

**Table 3:** Correlation coefficient of SBR with first and second IPs for metals containing positive BDE differences between  $[M-F]^+$  and  $[M-O]^+$ .

	SBR of $[M-F]^+$ with first IPs of metals	SBR of $[M-F]^+$ with second IPs of metals
Pearson correlation	-0.937	-0.973
P-value	0.019	0.005
$R^2$	0.88	0.95



**Figure 6:** Calibration graph of  $[\text{Ba-F}]^+$  with three different fluoride solutions: NaF, KF and HF.

In order to achieve low detection limits for fluorine and make its detection less matrix dependent,  $\text{F}^-$  should be directly detected. This could be achieved by two hypotheses:

- transferring  $\text{F}^-$  into the reaction cell of the ICPMS/MS and transfer the negative ion into a positive one  $[\text{X-F}]^+$  or
- detecting  $\text{F}^-$  in a negative ion mode ICPMS/MS.

Even though option (a) would be possible with any current commercial ICPMS/MS but very unlikely to be achieved. This is because it is difficult to find any reactive gases capable to form doubly charge ions, which react with  $\text{F}^-$  to form a polyatomic positive ion. Hence, it would be more likely to rebuild an ICPMS/MS with negative mode detection to achieve a more robust detection with limits of detection in the lower ppb or even sub-ppb range.

With today's technology of ICPMS in ion transmission and interferences removal, the negative ICPMS/MS has high potential in detecting not only halogens but also other negative ions such as nitrogen. Data from Vickers et al.<sup>6</sup> have been used to estimate the detection limit of fluorine by using the chlorine value as reference. In 1988, chlorine could be detected with three times better sensitivity in negative compared to positive mode. By considering the detection limit of chlorine with today's ICPMS/MS sensitivity ( $4.0 \mu\text{g/L}$ ),<sup>15,16</sup> it is expected that detection limits of chlorine and fluorine in lower to sub ppb range could be achieved in negative mode ICPMS/MS. Furthermore, interferences  $[\text{O}^{18}\text{H}]^-$  which impaired the fluorine detection in negative ion mode of the old ICPMS can now be reduced using reaction gas in collision/reaction cell.

ICPMS/MS in negative mode has a great potential for halogens detection which simultaneously could solve many problems in environmental and food analysis. Although, ion chromatography and ion selective electrode are the common analytical tools used for fluoride analysis, it is impossible with those methods to detect organofluorines such as per- and polyfluorinated compounds. Since only targeted method such as ESI-MS/MS and limited

standards are available, many of the organofluorine compounds remain undetected which not only occur in fluorinated polymer compounds but also in pharmaceutical application. Nowadays, almost 20% of all new pharmaceutical products are fluorinated.<sup>17</sup> The metabolism of those compounds cannot easily be studied due to mass balance problems when only molecular mass spectrometry is used. The same issue is further extended to chlorinated compounds and again, mass balance approaches for the biodegradation of chlorinated pesticides or insecticides or the metabolism of chlorinated pharmaceuticals can only be studied when an element-specific detector such as ICPMS is used for non-targeted analysis of body fluids or soil/plant extracts. Therefore, building a new negative-ion ICPMS would not only benefit the organofluorine polymer industry and the pharmaceutical sector but would also serve other communities such as scientist interested in environmental monitoring of fluorinated and chlorinated compounds.

### Conclusion:

In this work, the formation of fluorine-containing polyatomic ions with different metals using ICPMS/MS was demonstrated. High BDE of  $[M-F]^+$ , and relative low BDE of  $[M-O]^+$  together with a low second IP of the metal are the main features required by the metal to form  $[M-F]^+$  efficiently in an argon plasma. Ba has the highest sensitivity showed the most promising metal forming fluorine-containing polyatomic ions. The study revealed that  $M^{2+}$  harvesting  $F^-$  in the argon plasma to form  $[M-F]^+$  was the predominant process. Although this approach made it possible to detect fluorine in the sub-ppm concentration with ICPMS/MS, polyatomic ion formation is unstable and matrix dependent. A negative ion ICPMS/MS would be able to push the limits of detection to sub-ppb levels and with potentially less matrix effects. Negative ions ICPMS/MS would not only useful to detect halogens with low detection limit but also as an element-specific detector for identifying unknown halogens compounds from environment, food and/or pharmaceutical area.

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### References:

- 1 N. Yamada, in *Agilent 8800 ICP-QQQ Application Handbook*, Agilent Technologies, second edi., 2015, pp. 38–39.
- 2 W. Guo, L. Jin, S. Hu and Q. Guo, *J. Agric. Food Chem.*, 2017, **65**, 3406–3412.
- 3 Y. Z. Hu, K. N. Akano and Y. S. Hikamori, *Anal. sc*, 2017, **33**, 1279.
- 4 N. L. A. Jamari, J. F. Dohmann, A. Raab, E. M. Krupp and J. Feldmann, *J. Anal. At. Spectrom.*, 2017, **32**, 942–950.
- 5 N. L. A. Jamari, J. F. Dohmann, A. Raab, E. M. Krupp and J. Feldmann, *Prep.*, 2017.
- 6 G. H. Vickers, D. A. Wilson and G. M. Hieftje, *Anal. Chem.*, 1988, **60**, 1808–1812.
- 7 M. Chtaib and J.-P. Schmit, *J. Anal. At. Spectrom.*, 1988, **3**, 315–318.
- 8 S. R. Langhoff, C. W. Bauschlicher and H. Partridge, *J. Chem. Phys.*, 1986, **84**, 1687–

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60
- 1 1695.
- 2 9 K. Schofield, *Chem. Rev.*, 1967, **67**, 707–715.
- 3 10 H. Partridge, S. R. Langhoff and C. W. Bauschlicher, *J. Chem. Phys.*, 1986, **84**, 4489–  
4 4496.
- 5 11 R. J. Ackermann, E. G. Rauh and R. J. Thorn, *J. Chem. Phys.*, 1976, **65**, 1027.
- 6 12 L. A. Kaledin, M. C. Heaven and R. W. Field, *J. Mol. Spectrosc.*, 1999, **193**, 285–292.
- 7 13 J. A. Olivares and R. S. Houk, *Anal. Chem.*, 1986, **58**, 20–25.
- 8 14 D. A. Wilson, G. H. Vickers, G. M. Hieftje and A. T. Zander, *Spectrochim. Acta Part B At.*  
9 *Spectrosc.*, 1987, **42**, 29–38.
- 10 15 N. Sugiyama, *Trace level analysis of sulfur, phosphorus, silicon and chlorine in NMP*  
11 *using the Agilent 8800 Triple Quadrupole ICP-MS*, Tokyo, Japan, 2013.
- 12 16 B. Divjak, M. Novič and W. Goessler, *J. Chromatogr. A*, 1999, **862**, 39–47.
- 13 17 A. Harsanyi and G. Sandford, *Green Chem.*, 2015, **17**, 2081–2086.

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## Table of Entry

The paper describes that the 2<sup>nd</sup> ionisation potential and the difference in bond energy of a metal to fluorine and of metal to oxygen are the most important parameter to form a metal fluoride ion for the detection of fluorine in an ICPMS/MS.

