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# Plasma processes to detect fluorine with ICPMS/MS as $[M\text{-}F]^+$: an argument for building a negative mode ICPMS/MS

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## Supplementary Information

**Table S1**: Optimum instrument settings for determination of $[M\text{-}F]^+$.

| **Metal (M)** | Ba | Sr | Eu | Ca | Yb | Er* | Gd* | Ce* | La* | Pr* |
|---|---|---|---|---|---|---|---|---|---|---|
| **Plasma** | | | | | | | | | | |
| RF Power / W | 1500 | 1500 | 1600 | 1500 | 1600 | 1200 | 1600 | 1200 | 1600 | 1400 |
| Sampling Position / mm | 8.5 | 10.0 | 7.5 | 14.5 | 12.5 | 10.0 | 7.5 | 13.0 | 10.5 | 14.5 |
| Nebulizer gas flow rate / L/min | 1.0 | 1.0 | 1.0 | 0.96 | 1.02 | 0.96 | 0.84 | 1.0 | 0.9 | 1.0 |
| Makeup gas flow rate / L/min | 0.36 | 0.42 | 0.36 | 0.38 | 0.32 | 0.28 | 0.3 | 0.3 | 0.4 | 0.3 |
| **Cell** | | | | | | | | | | |
| Oxygen flow rate / mL/min | 0.75 | 0.4 | 0.6 | 1.0 | 0.7 | 0 | 0 | 0.8 | 0.6 | 0.5 |

*optimisation based on the sensitivity of $[M\text{-}F]^+$ was limited due to the negative value of signal-to-background ratio (SBRs)

**Calculation of signal-to-background ratio (SBR) and corrected SBR of $[M\text{-}F]^+$**

$$SBR\ of\ [M-F]^+ = \frac{I_F - I_{blank}}{I_{blank}}$$

$$Corrected\ SBR\ of\ [M-F]^+ = \frac{SBR\ of\ [M-F]^+}{isotopic\ fraction}$$

Remarks:
$I_{blank}$ intensity of *m/z* 157 without fluorine containing solution
$I_F$ intensity of *m/z* 157 with fluorine containing solution

**Bond dissociation energy (BDE) of different metals with fluorine $[M\text{-}F]^+$ and oxygen $[M\text{-}O]^+$.**

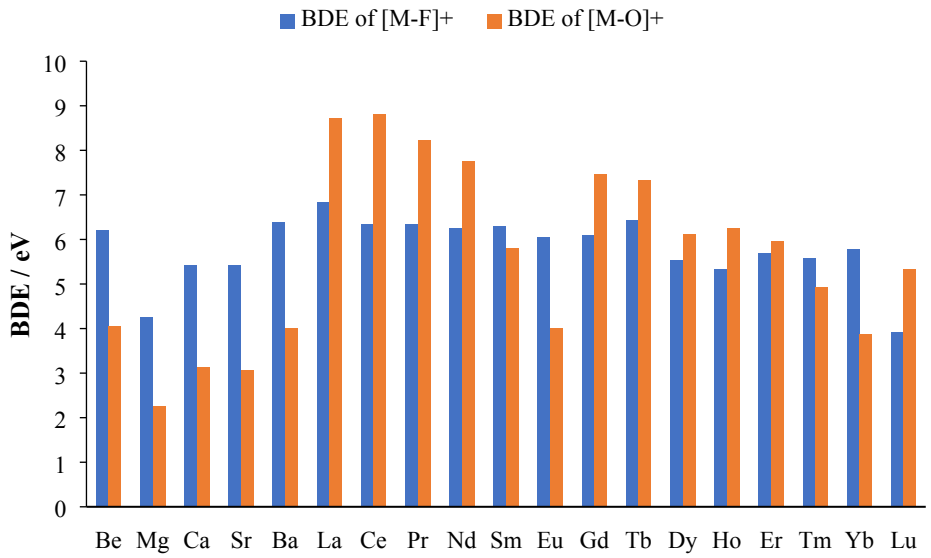


**Figure S1**: The BDE of metals with fluorine $[M\text{-}F]^+$ and oxygen $[M\text{-}O]^+$.

**Different Ba concentration**

The SBR of $[Ba\text{-}F]^+$ increase with increasing Ba concentrations between 10-100 mg/L. However, the counts barely increase from 50 to 100 mg/L, hence 50 mg/L of Ba is reasonable to be use to avoid clogging on the sampler and/or skimmer cone.

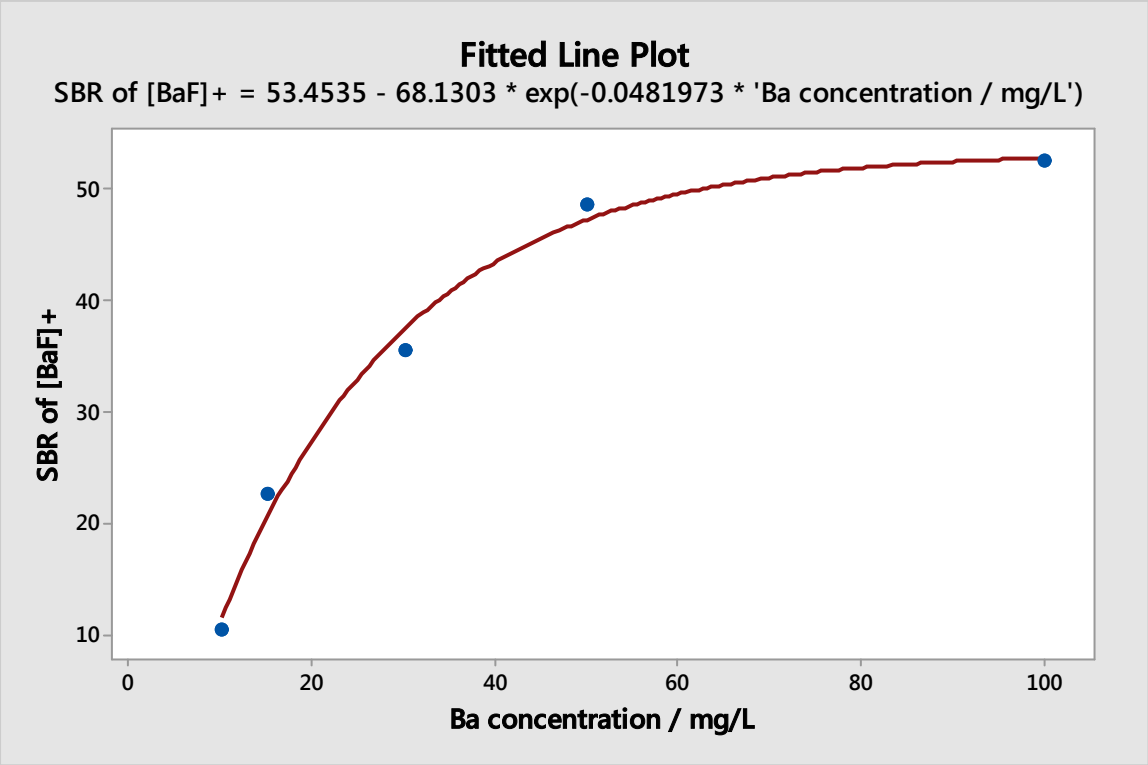


**Figure S2:** An asymptotic graph of the sensitivity of $[Ba\text{-}F]^+$ at different Ba concentrations.

**Sensitivity of $[M\text{-}F]^+$ versus first and second IP**

The sensitivity of $[M\text{-}F]^+$ was calculated based on molarity of measured isotope.

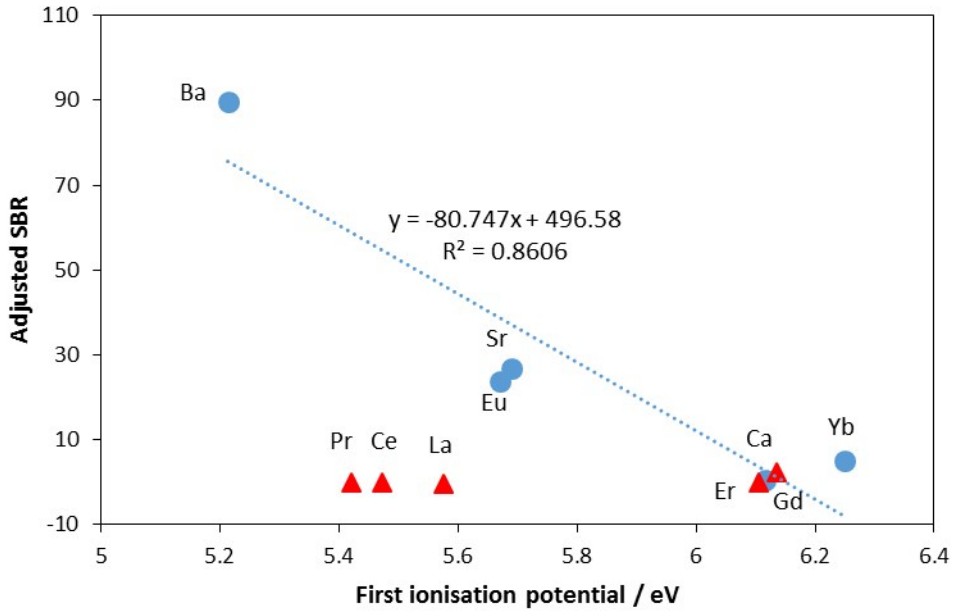


**Figure S3a:** Adjusted SBR based on molarity of measured isotope for first IP of different metals.

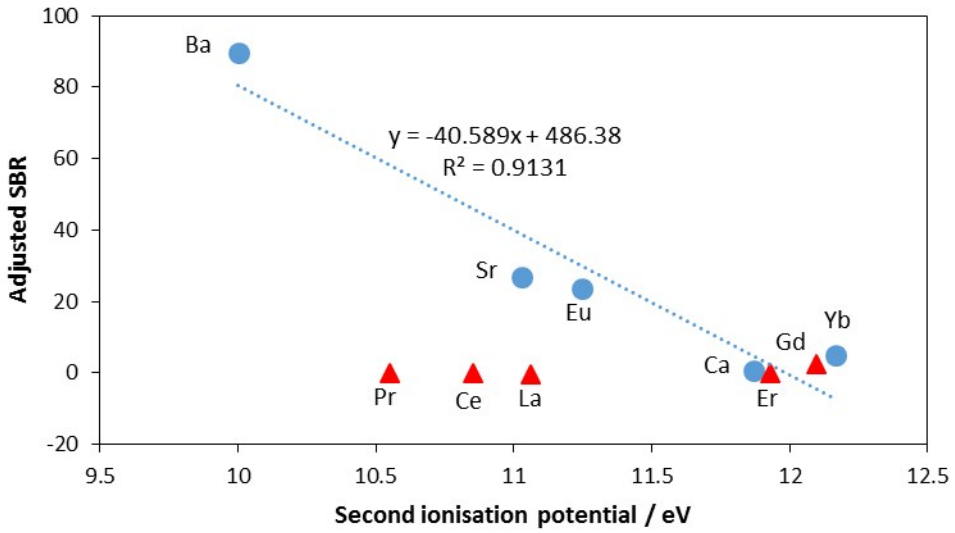


**Figure S3b:** Adjusted SBR based on molarity of measured isotope for second IP of different metals.

**Stability of $[M\text{-}F]^+$ formation**

The bar chart shows the average SBR of $[M\text{-}F]^+$ for Ba, Sr and Eu at three different days. The most promising metal to form $[M\text{-}F]^+$ is Ba as it has the highest SBR. Even though Sr exhibit smaller error compared to Ba, Sr always form precipitates inside the torch which require a cleaning after each measurement.

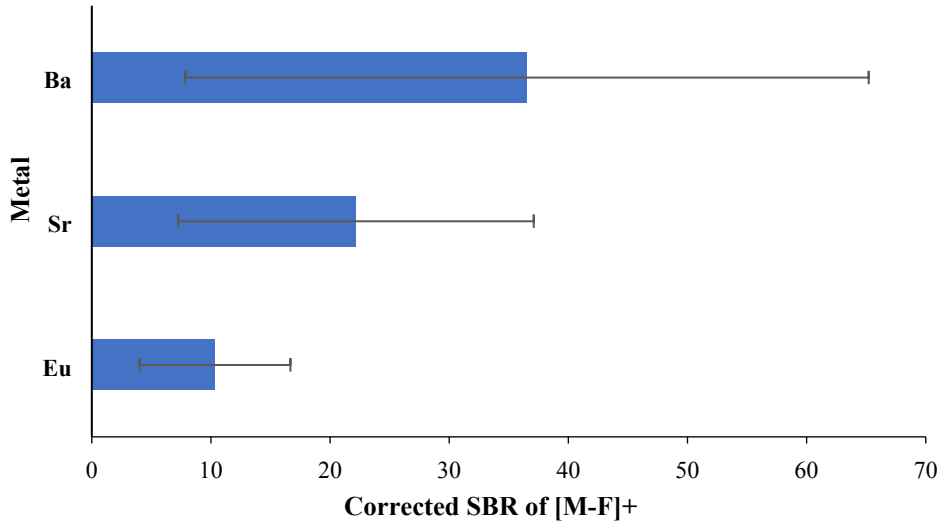


**Figure S4:** The average SBR of $[M\text{-}F]^+$ for Ba, Sr and Eu measured at three different days under the optimum condition.

## Matrix effect

The signal of $[Ba\text{-}F]^+$ with two different fluorine solutions. The sensitivity is much higher from potassium fluoride (KF) compared to hydrogen fluoride (HF) indicating there is signal enhancement coming from potassium (K). In order to study the matrix effect, different concentration of cations, anions and methanol were introduced to Ba and F solution. The sensitivity of $[Ba\text{-}F]^+$ highly dependent on cations but no effect were seen from anions or methanol.

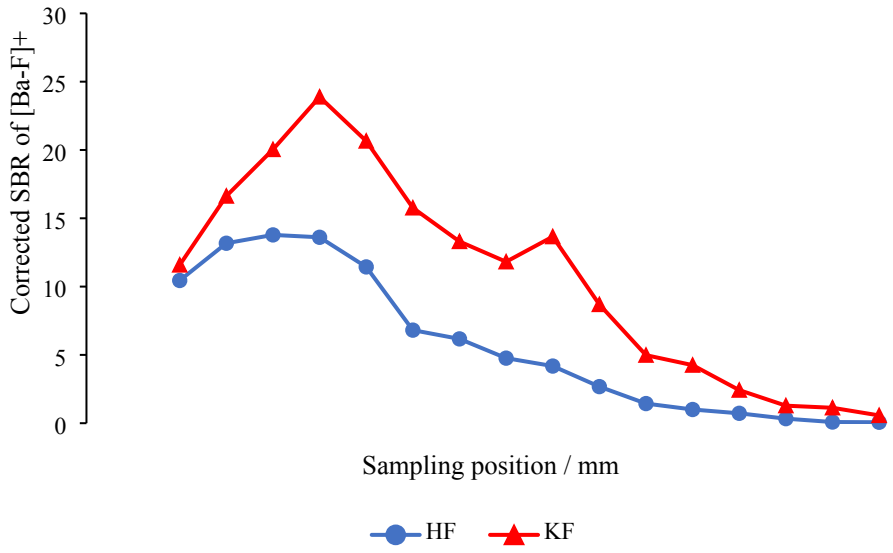


**Figure S5:** The corrected SBR of $[Ba\text{-}F]^+$ in two fluorine solutions (approximately 10 mg F/L): potassium fluoride, KF (blue circle) while hydrogen fluoride, HF (red triangle) at different sampling position.

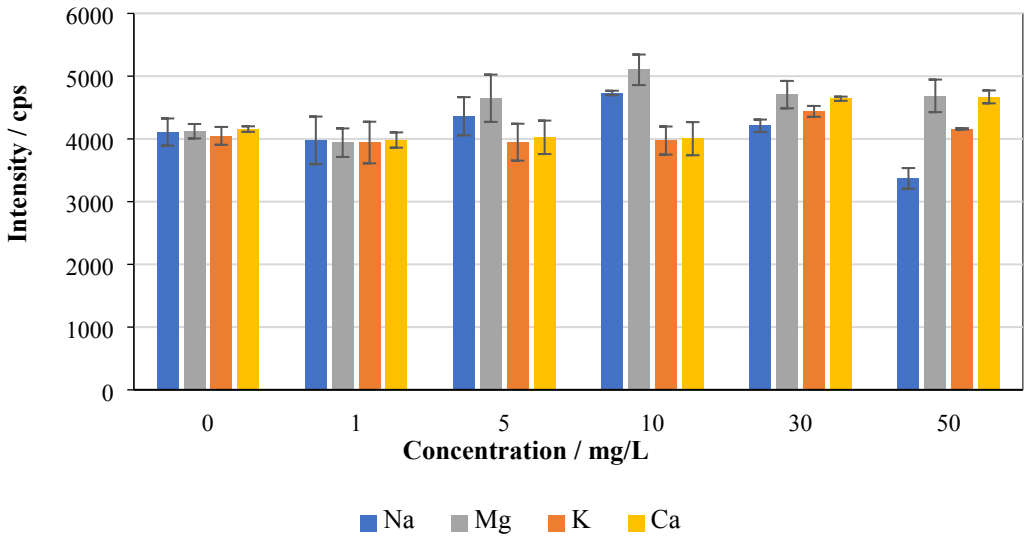


**Figure S6:** Influence of the Na, Mg, K and Ca concentration on the $[Ba\text{-}F]^+$ signal intensity.

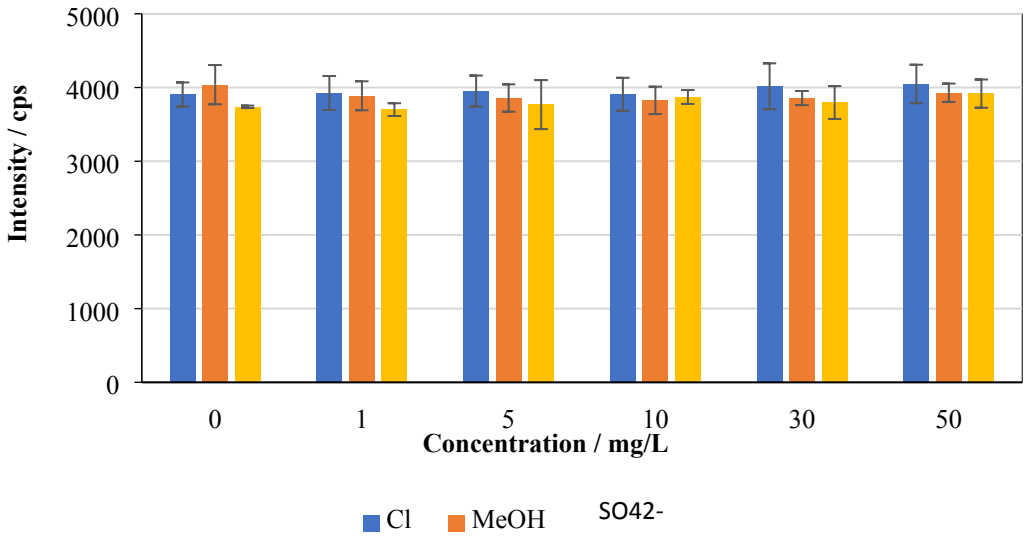


**Figure S7:** Influence of the $Cl^-$, $SO_4^{2-}$ and methanol concentration on the $[Ba\text{-}F]^+$ signal intensity.