Electronic Supplementary Information

NOVEL NON-TARGET ANALYSIS FOR FLUORINE COMPOUNDS USING ICPMS/MS AND HPLC-ICPMS/MS

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Reaction gas

Different gas modes for the collision/reaction cell of the ICPMS/MS were investigated. A high F sensitivity and signal-to-background ratio (SBR) for BaF$^+$ was observed for O_2 as reaction gas.

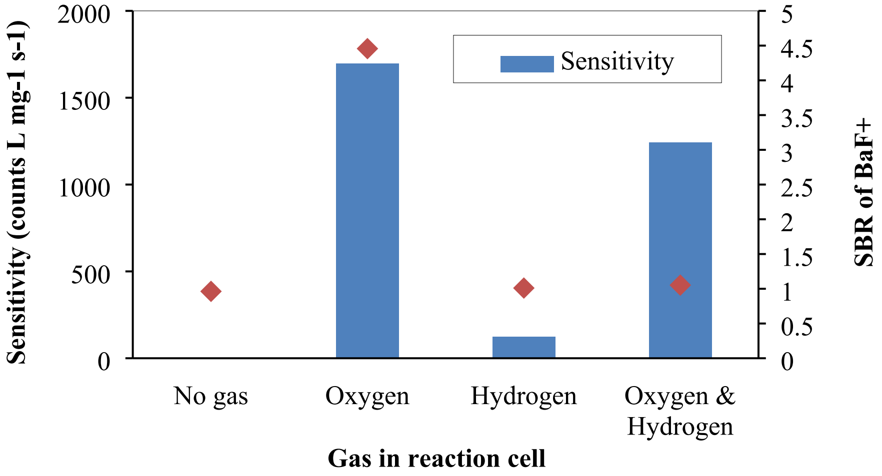


Fig. ESI-1 The effects of different gas modes use in reaction cell on $^{138}Ba^{19}F^+$ formation. The sensitivity based on the slope of calibration graph of *m/z* 157 (bars); SBR for $^{138}Ba^{19}F^+$ between 2.5 mg L^{-1} F containing solution to blank are illustrated as diamonds. Highest sensitivity and best SBR for $^{138}Ba^{19}F^+$ is observed for oxygen as reaction cell gas.

Product Ion Scan

A product ion scan of ions with *m/z* 157 has been carried out. Product ions with *m/z* 32, 138, 154, 155 and 170 are believed the result from interfering ions such as $^{138}Ba^{18}O^{1}H^{+}$, $^{138}Ba^{17}O^{2}H^{+}$, and $^{138}Ba^{16}O^{1}H_3{}^{+}$, as the intensities for those product ions ($^{16}O^{16}O^{+}$, $^{138}Ba^{+}$, $^{138}Ba^{16}O^{+}$, $^{138}Ba^{16}O^{1}H$ and $^{138}Ba^{16}O_2{}^{+}$) are independent of the introduced fluoride concentration as shown in Fig. ESI-2.

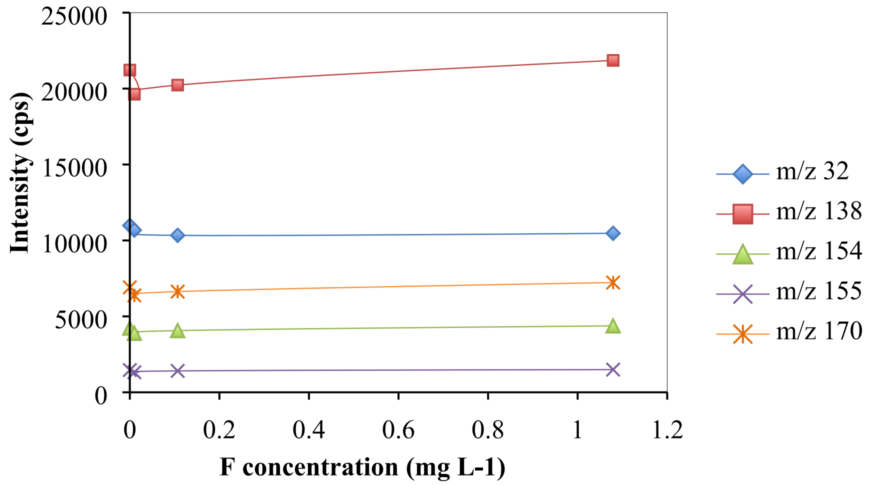


Fig. ESI-2 The effect on product ions counts *m/z* 32, 138, 154, 155 and 170 in the presence of different F concentrations. No correlation between F concentration and signal intensity could be observed.

Schematic diagram of MS/MS

The capability of MS/MS in eliminating interferences was displayed in the schematic diagram below. The first quadrupole (Q_1) act as mass filter to eliminate all ions except the target mass ions (*m/z* 157). Meanwhile, the interferences that has the same mass as the target ions could be eliminate using reaction gas ie. oxygen in collision/reaction cell.

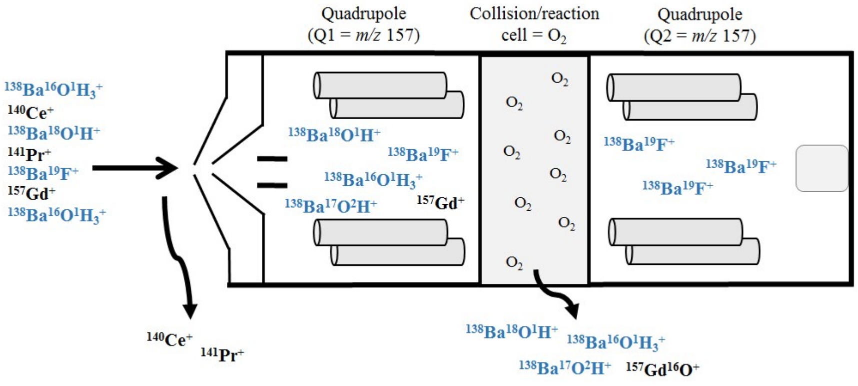


Fig. ESI-3 Schematic diagram of MS/MS in eliminating interference of non-target ions. Q_1 eliminate all ions except the target mass ions (*m/z* 157), while oxygen as reaction gas eliminates the interferences that have the same mass as target ions ($^{157}Gd^{+}$, $^{138}Ba^{18}O^{1}H^{+}$, $^{138}Ba^{17}O^{2}H^{+}$ and $^{138}Ba^{16}O^{1}H_3{}^{+}$).

Sample position

Fig. ESI-4 shows the raw data for the measured intensities for blank and F containing solution (5 mg L^{-1}). The result shows a maximum intensity at low sample position and a secondary maximum intensity at approximately 18.0 mm. The existence of two different maxima possibly indicates the formation of BaF$^+$ in different mechanism. The sampling position that gives the higher maximum in background subtraction (8 mm) was chosen as it shows more efficient formation mechanism for BaF$^+$.

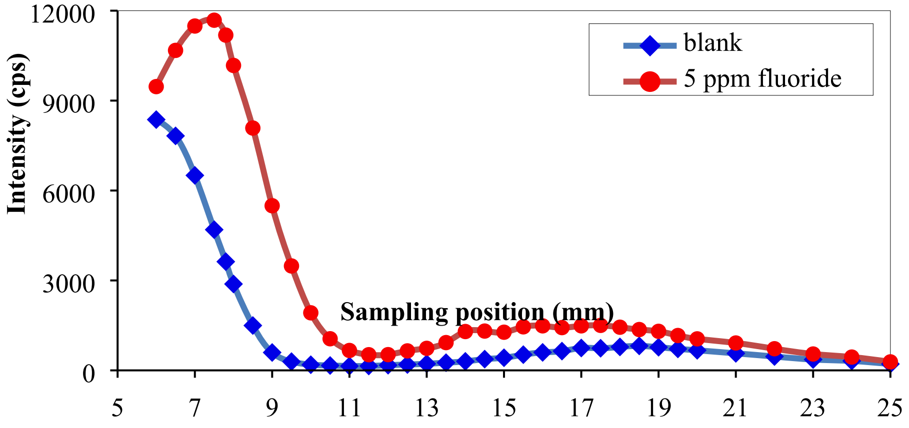


Fig. ESI-4 Measured intensities for blank and F containing solution (5 mg L^{-1}) dependant on the sampling position.

Acquisition time

Different acquisition time on $^{138}Ba^{19}F^+$ counts using 10 replicates for each measurement and wait time offset were evaluated for the possibility of better signal acquisition. The SD of the measurement improved as the acquisition time increase and no significant effect of different wait time offset (WTO) on $^{138}Ba^{19}F^+$ counts (Fig. ESI-5 and ESI-6). For further analysis, 1.0 s acquisition time and 2 ms wait time offset were used to give adequate time for acquisition and reaction.

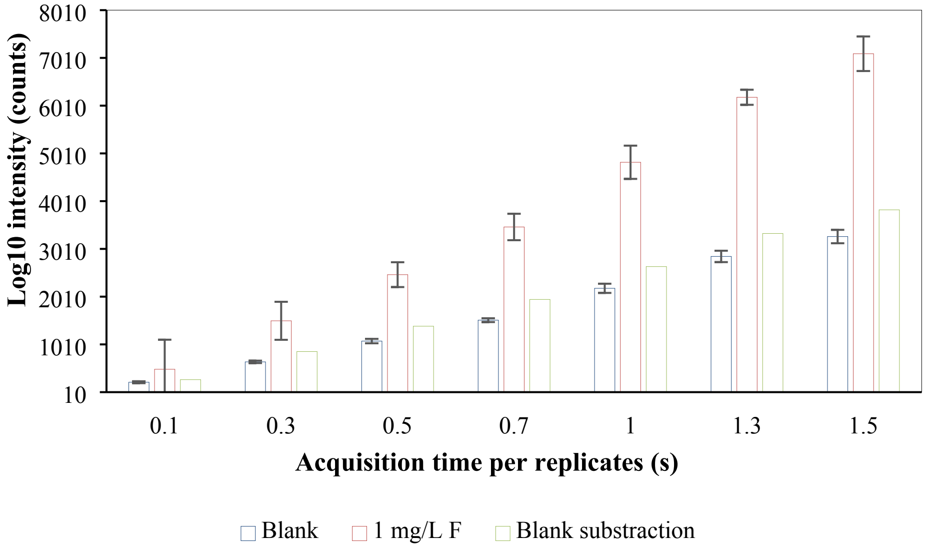


Fig. ESI-5 Log$_{10}$ intensity of *m/z* 157 counts as a function of acquisition time per replicates in blank and 1 mg L^{-1} F containing solution. Each measurement was done with 10 replicates measurement. $^{138}Ba^{19}F^{+}$ counts increase as the acquisition time increased with improved in SD.

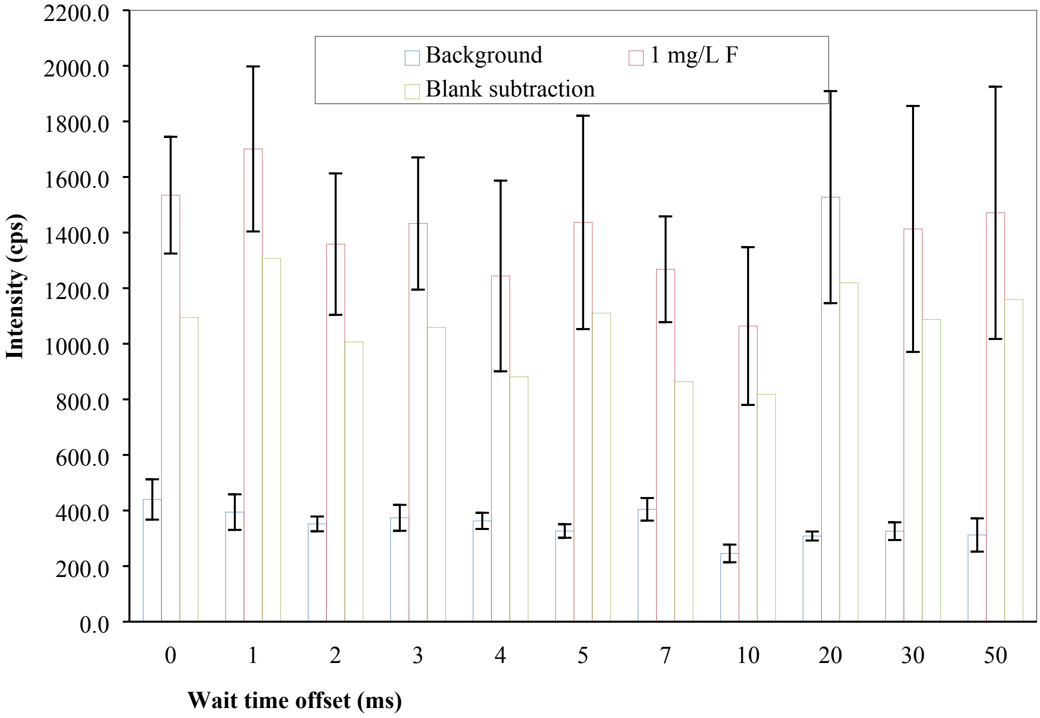
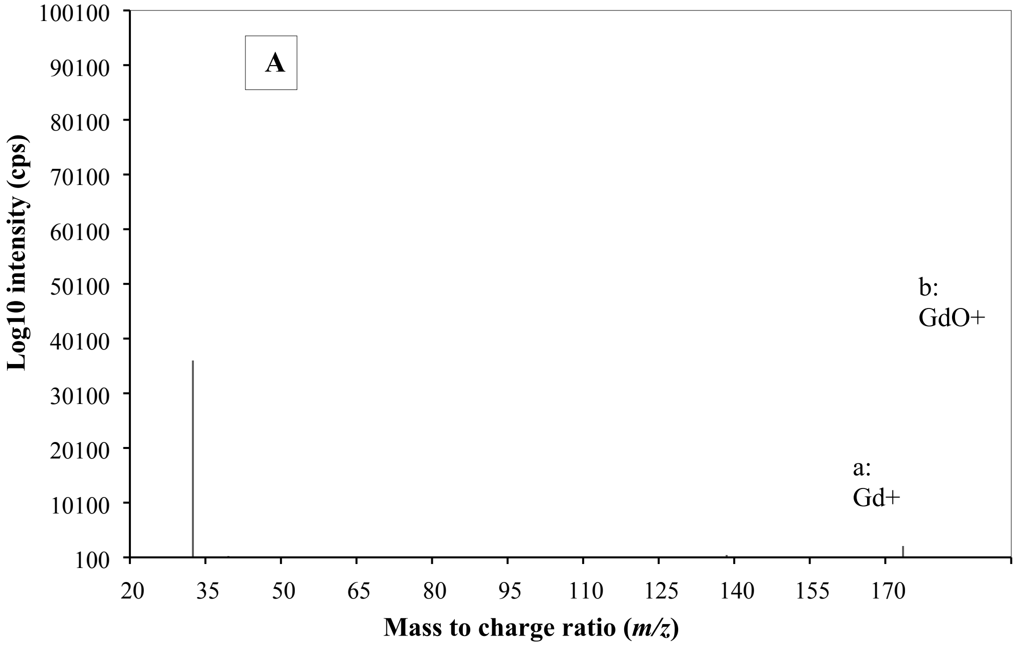


Fig. ESI-6 Intensity of *m/z* 157 as a function of wait time offset obtained using 1 s of acquisition time in blank solution and 1 mg L^{-1} F. No significant effect on the $^{138}Ba^{19}F^{+}$ intensities.

Product ion scan of Gd

The capability of the BaF$^+$ optimised method to remove interference of Gd was evaluated through product ion scan of $^{157}Gd^+$ at *m/z* 157. Small traces of Gd$^+$ was detected on *m/z* 157, while majority of Gd$^+$ was oxidised in the collision/reaction cell by oxygen to $^{157}Gd^{16}O^+$ at *m/z* 173.



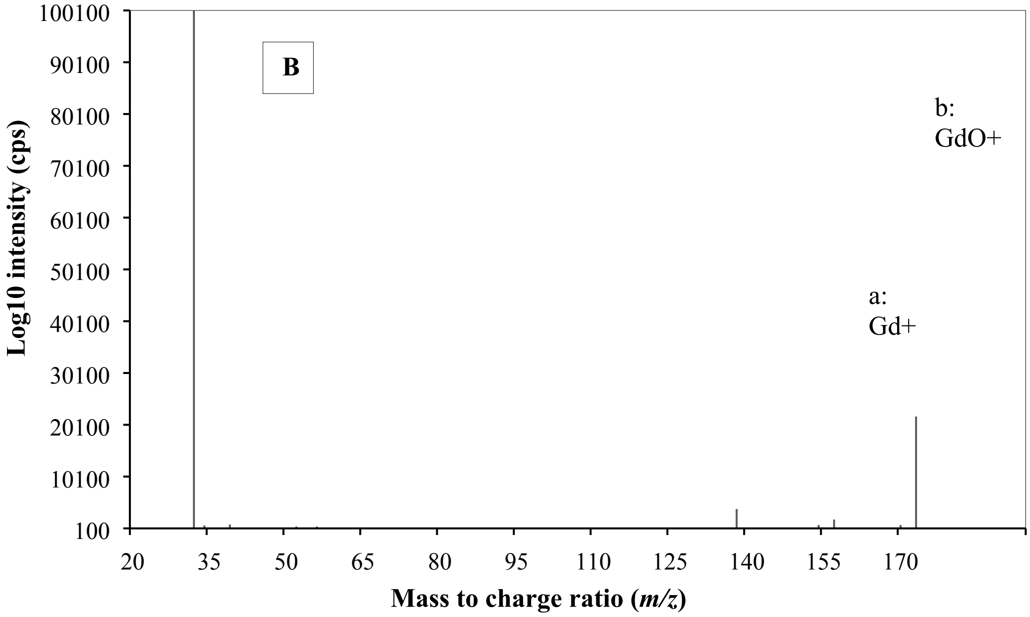


Fig. ESI-7 MS/MS spectra: The reaction product ion scan of Gd at *m/z* 157 using BaF$^+$ optimised method in (A) blank and (B) 100 µg L^{-1} Gd solution. (a) *m/z* 157 being $^{157}Gd^+$ and (b) *m/z* 173 being $^{157}Gd^{16}O^+$.

Statistical analysis

In order to check whether mean concentration measured by ICPMS/MS differ from the concentration the added to deionised water, statistic *t*-test was conducted. The result indicates that both mean concentration is similar.

Table ESI-1 *t*-test analysis with 95% confidence interval (CI) for F concentration spiked into deionised water and the concentration measured by ICPMS/MS.

Sample	N	Mean ± SD	T-value	P-value
Concentration spiked into deionised water	3	0.98 ± 0.040	0.80	0.48
Concentration measured by ICPMS/MS	3	0.95 ± 0.058		

The robustness and reliability of the ICPMS/MS method was evaluated by observing the RSD on sample triplicates measurement as well as the RSD on 10 replicates in each measurement. The results show a low RSD for both analysis demonstrating the method can be trusted and use in further analysis.

Table ESI-2 The RSD of spiked F in deionised water based on three measurements and 10 replicates in each measurement as a function of reproducibility of the method.

F spike in deionised water	RSD of measurement (%)	RSD of 10 replicates (%)
Spike 1	5.8	2.4
Spike 2		2.4
Spike 3		3.1

t-test analysis was conducted to determine whether mean concentration measured by HPLC-ICPMS/MS differ from the concentration the added to deionised water. The result indicates that both mean concentrations for each F compound are similar.

Table ESI-3 *t*-test analysis for fluoride and fluoroacetate concentration spiked into deionised water and the concentration measured by ICPMS/MS with 95% confidence interval.

F compound	Sample	N	Mean ± SD	T-value	P-value
Fluoride	Concentration spiked into deionised water	3	0.97 ± 0.023	0.76	0.53
	Concentration measured by ICPMS/MS	3	0.93 ± 0.083		
Fluoroacetate	Concentration spiked into deionised water	3	0.99 ± 0.029	1.68	0.23
	Concentration measured by ICPMS/MS	3	0.90 ± 0.087		

Calculation of LODs and LOQs

The LODs was calculated from 3SD of blank value, while LOQs was calculated from 10SD of blank value based on the linear equation of calibration graph.

$$LOD = \frac{((3 * SD\ of\ blank\ value) + (average\ of\ blank\ value)) - intercept}{slope}$$

$$LOQ = \frac{((10 * SD\ of\ blank\ value) + (average\ of\ blank\ value)) - intercept}{slope}$$

ICPMS/MS

Average of blank value	1960.0
SD of blank value	19.8
Slope	3229.1
Intercept	1881.7

$$LOD = \frac{((3 * 19.8) + (1960)) - 1881.7}{3229.1} = 0.043\ mg/L$$

$$LOQ = \frac{((10 * 19.8) + (1960)) - 1881.7}{3229.1} = 0.086\ mg/L$$

HPLC-ICPMS/MS

a) **For fluoride**

Average of blank value	3665.3
SD of blank value	218.5
Slope	24474.4
Intercept	3774.3

$$LOD = \frac{((3 * 218.5) + (3665.3)) - 3774.3}{24474.4} = 0.022\ mg/L$$

$$LOQ = \frac{((10 * 218.5) + (3665.3)) - 3774.3}{24474.4} = 0.085\ mg/L$$

b) For FAA

Average of blank value	4625.7
SD of blank value	216.1
Slope	23993.4
Intercept	2545.3

$$LOD = \frac{((3 * 216.1) + (4625.7)) - 2545.3}{23993.4} = 0.11\ mg/L$$

$$LOQ = \frac{((10 * 216.1) + (4625.7)) - 2545.3}{23993.4} = 0.18\ mg/L$$