

## Introduction

Phosphorus (<sup>31</sup>P) is one of the most difficult elements to analyze at low concentrations by conventional single quadrupole ICP-MS (ICP-QMS), because of interference from polyatomic ions such as NO<sup>+</sup> (<sup>15</sup>N<sup>16</sup>O<sup>+</sup>, <sup>14</sup>N<sup>17</sup>O<sup>+</sup>) and <sup>14</sup>N<sup>16</sup>OH<sup>+</sup> at *m/z* 31. Recently, the BEC (Background Equivalent Concentration) that can be achieved for P has been drastically reduced by triple quadrupole ICP-MS (ICP-QQQ). Using a mass shift method with oxygen reaction cell gas, P is measured as PO<sup>+</sup>. The principle is based on the fact that the oxygen atom transfer reaction is exothermic for P<sup>+</sup>: P<sup>+</sup> + O<sub>2</sub> → PO<sup>+</sup> + O (Δ*H* = -3.1 eV[1]), but it is endothermic for the interfering ions: NO<sup>+</sup> + O<sub>2</sub> → NO<sub>2</sub><sup>+</sup> + O (Δ*H* = +2.48 eV[1]), and HNO<sup>+</sup> + O<sub>2</sub> → NO<sub>2</sub>H<sup>+</sup> + O (Δ*H* = +1.62 eV[1]) (see Fig.1). Therefore, oxygen mass shift method is very effective to resolve the interfering ions for analysis in aqueous samples.

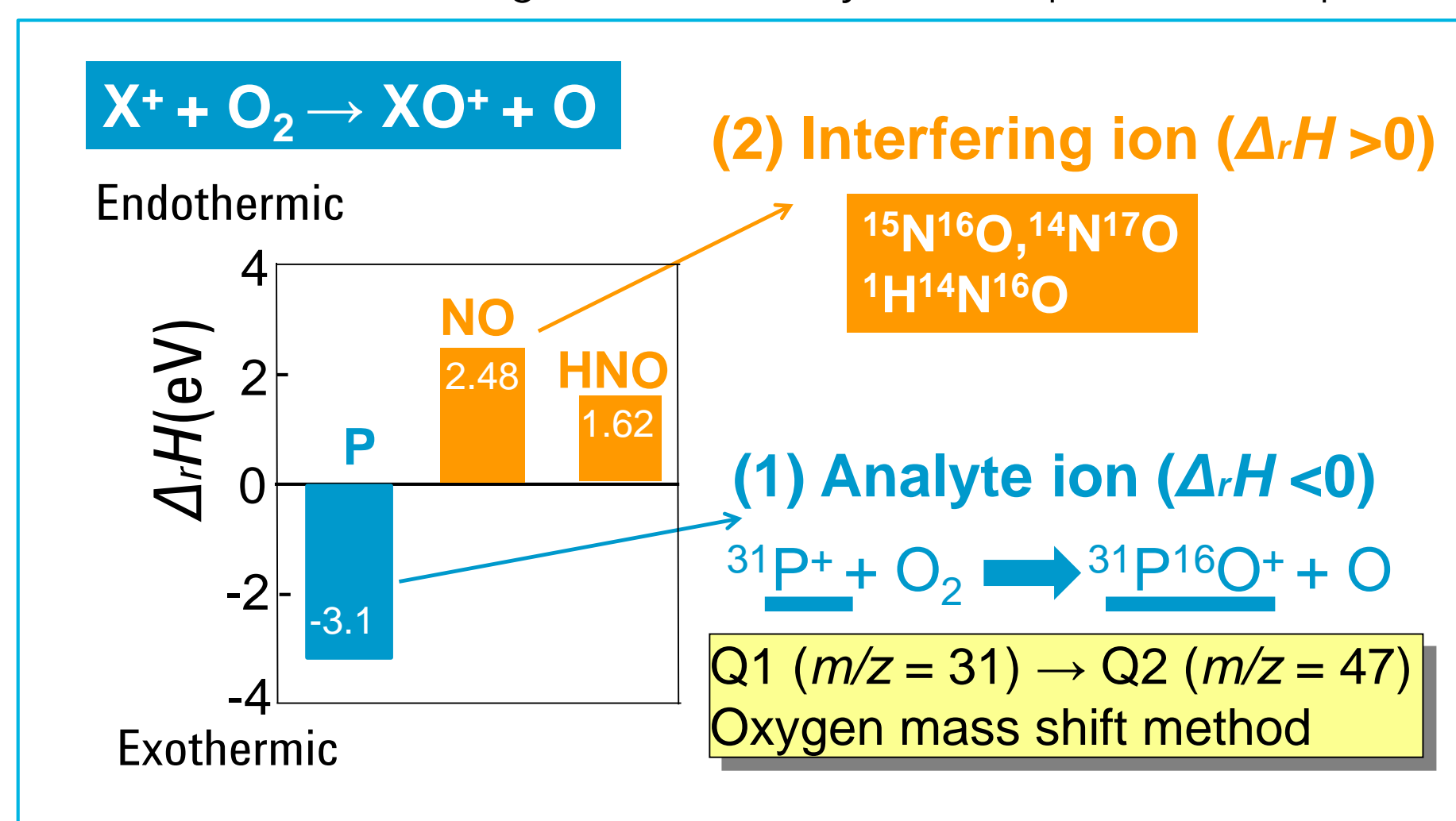


Figure 1 Δ*H* (heat of reaction) for O-atom transfer reaction of P<sup>+</sup>, NO<sup>+</sup> and NOH<sup>+</sup>

However, for organic solvents, P analysis is also affected by carbon-based interferences such as <sup>13</sup>C<sup>18</sup>O<sup>+</sup>, COH<sup>+</sup> (<sup>12</sup>C<sup>18</sup>OH<sup>+</sup>, <sup>13</sup>C<sup>17</sup>OH<sup>+</sup>), which also occur at *m/z* 31. In this study, a triple quadrupole ICP-MS (Agilent 8900) in MS/MS mode was used to investigate the BEC reduction mechanism for P in IPA (isopropyl alcohol). Two different reaction modes were studied, using oxygen and hydrogen cell gas.

## Experimental

**Instrumentation:** Agilent 8900 #200 (semiconductor configuration) was used with a 1.5 mm id quartz torch, quartz spray chamber and PFA nebulizer (MFN100). Samples were self-aspirated at a flow rate of 0.17 mL/min.

**Plasma conditions:** For <sup>31</sup>P (ionization Energy: 10.48 eV) measurement, hot plasma conditions were used. The plasma conditions are summarized in Table 1.

### Reagents and samples:

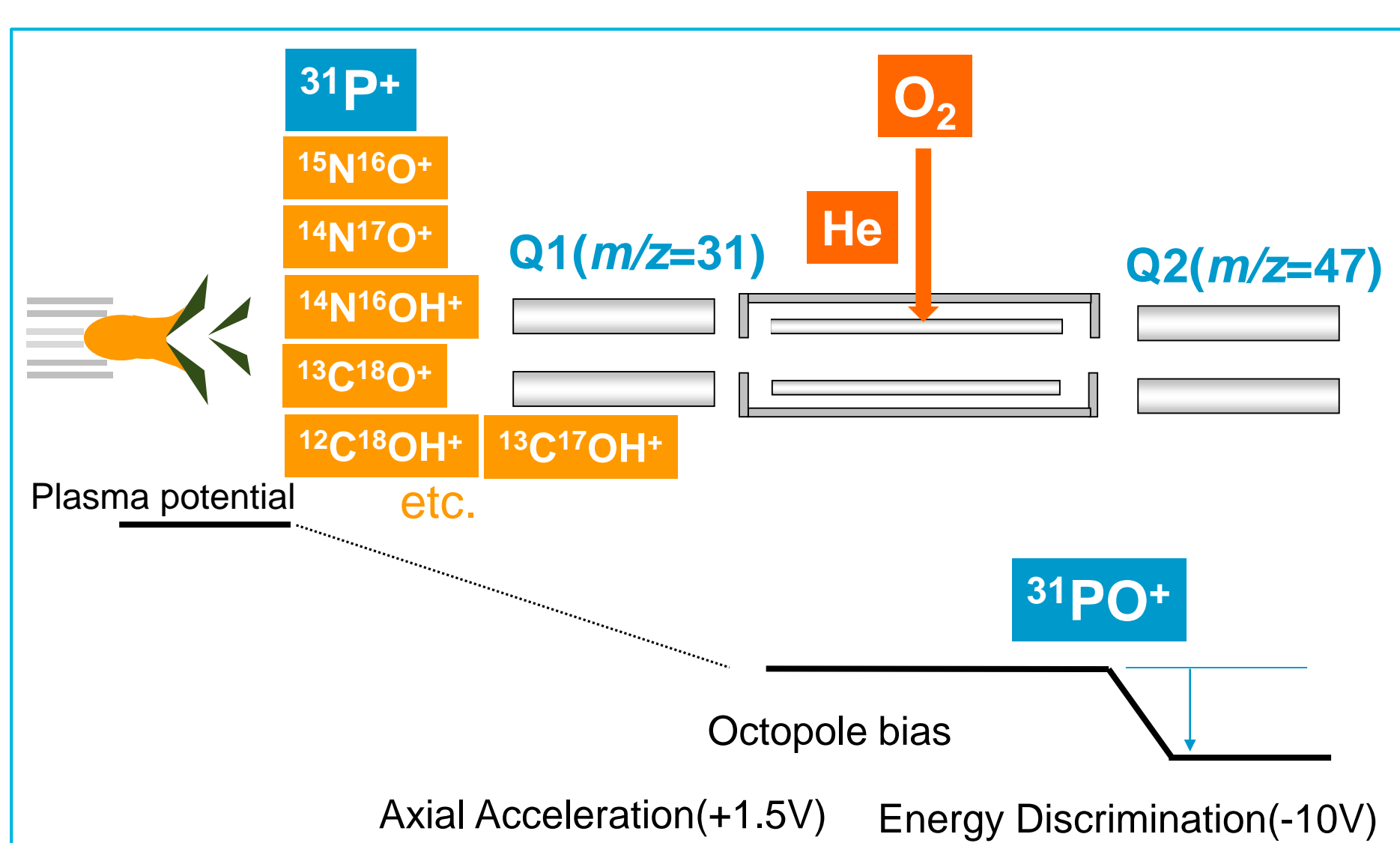
Sample: IPA (Electronic Grade).

Standard: SPEX aqua base phosphorus CRM (PLP9-3Y)

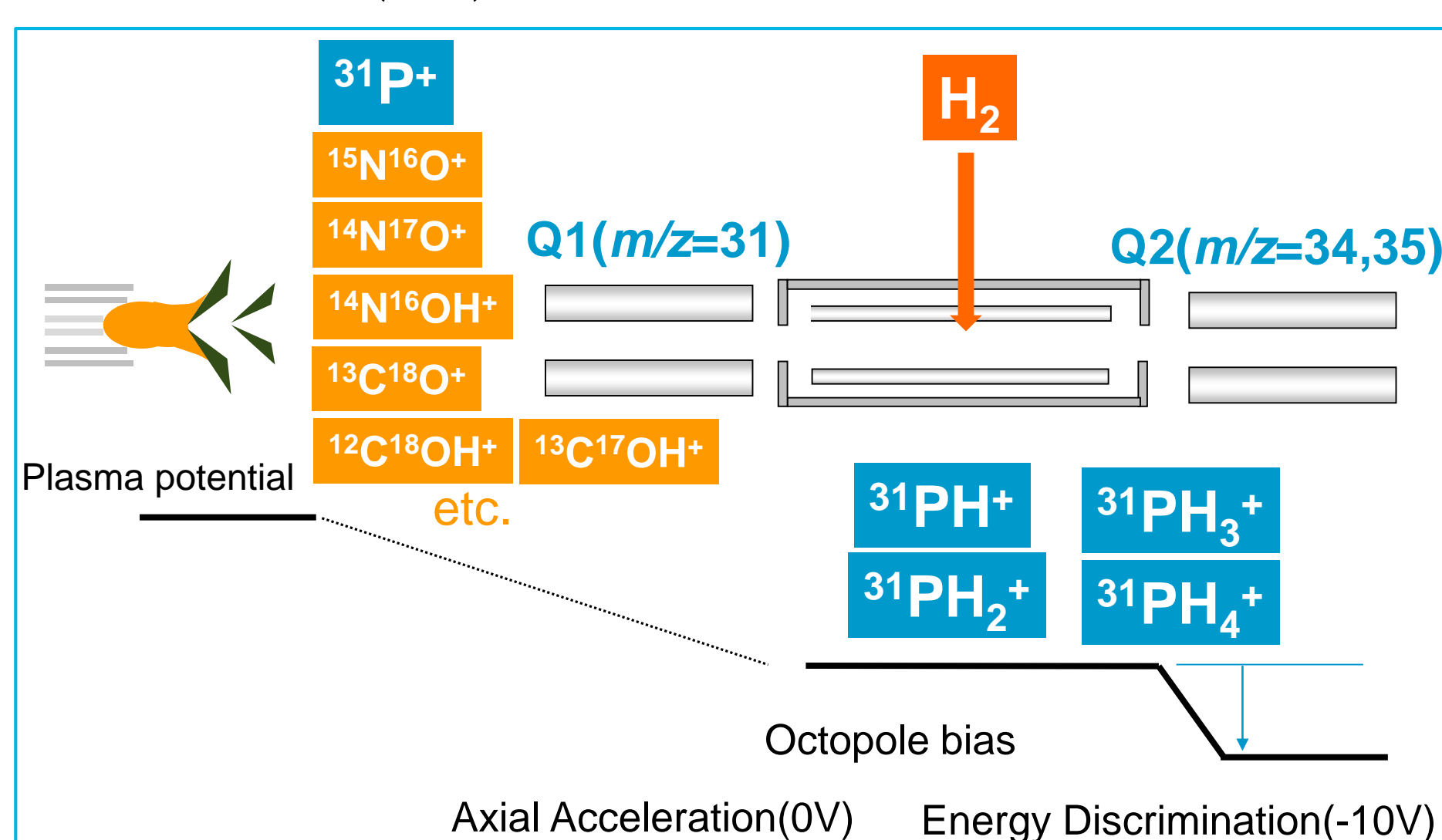
Table 1 Plasma Conditions (Agilent 8900)

Parameter	Unit	Value
RF	W	1500
Sampling Depth	mm	18
Carrier Gas flow	L/min	0.7
Make up Gas flow	L/min	0.55
Option Gas flow(*)	L/min	0.25

\* Oxygen (20%)/Ar



(1) **Oxygen mass-shift mode**, where the product ion PO<sup>+</sup> is formed by reaction with O<sub>2</sub> cell gas. Q1 (an additional mass filter positioned in front of the collision/reaction cell) is set to *m/z* = 31 (P<sup>+</sup>) and Q2 (the analyzer mass filter positioned after the cell) is set to *m/z* = 47 (PO<sup>+</sup>)



(2) **Hydrogen mass-shift mode**, where hydride product ions (mainly PH<sub>3</sub><sup>+</sup> and PH<sub>4</sub><sup>+</sup>) are produced from the reactions with H<sub>2</sub> cell gas. Q1 is set to *m/z* = 31 (P<sup>+</sup>) and Q2 is set to *m/z* = 34 (PH<sub>3</sub><sup>+</sup>) and 35 (PH<sub>4</sub><sup>+</sup>)

Figure 2 Experimental diagrams for oxygen mass shift method (1) and hydrogen mass-shift method (2)

## Results and Discussion

### (1) Oxygen mass-shift mode (P measured as PO<sup>+</sup>)

Firstly, oxygen mode was investigated under different cell conditions. The BEC for P as a function of Octopole bias was measured with an O<sub>2</sub> flow rate of 0.45 ml/min (cell parameter set at 30% full scale of 1.5 mL/min) to find the optimum cell conditions as shown in Fig.3. When Octopole bias was changed, the deflect lens was also optimized to increase the sensitivity. When Octopole bias is at 0V, the minimum BEC of 0.082ppb for P was obtained with sensitivity of 9150cps/ppb. The BEC increased with decreasing Octopole bias (increasing collision energy) in the range from 0 to -20V, and reached the maximum (1.55ppb) at -20V, then it decreased again as the bias was decreased from -20V to -50V. While the BEC for P in IPA varied by more than one order of magnitude with Octopole bias, the BEC for P in 1% HNO<sub>3</sub> is almost independent of Octopole bias as shown in Fig.4 (0.056 ppb at 0V).

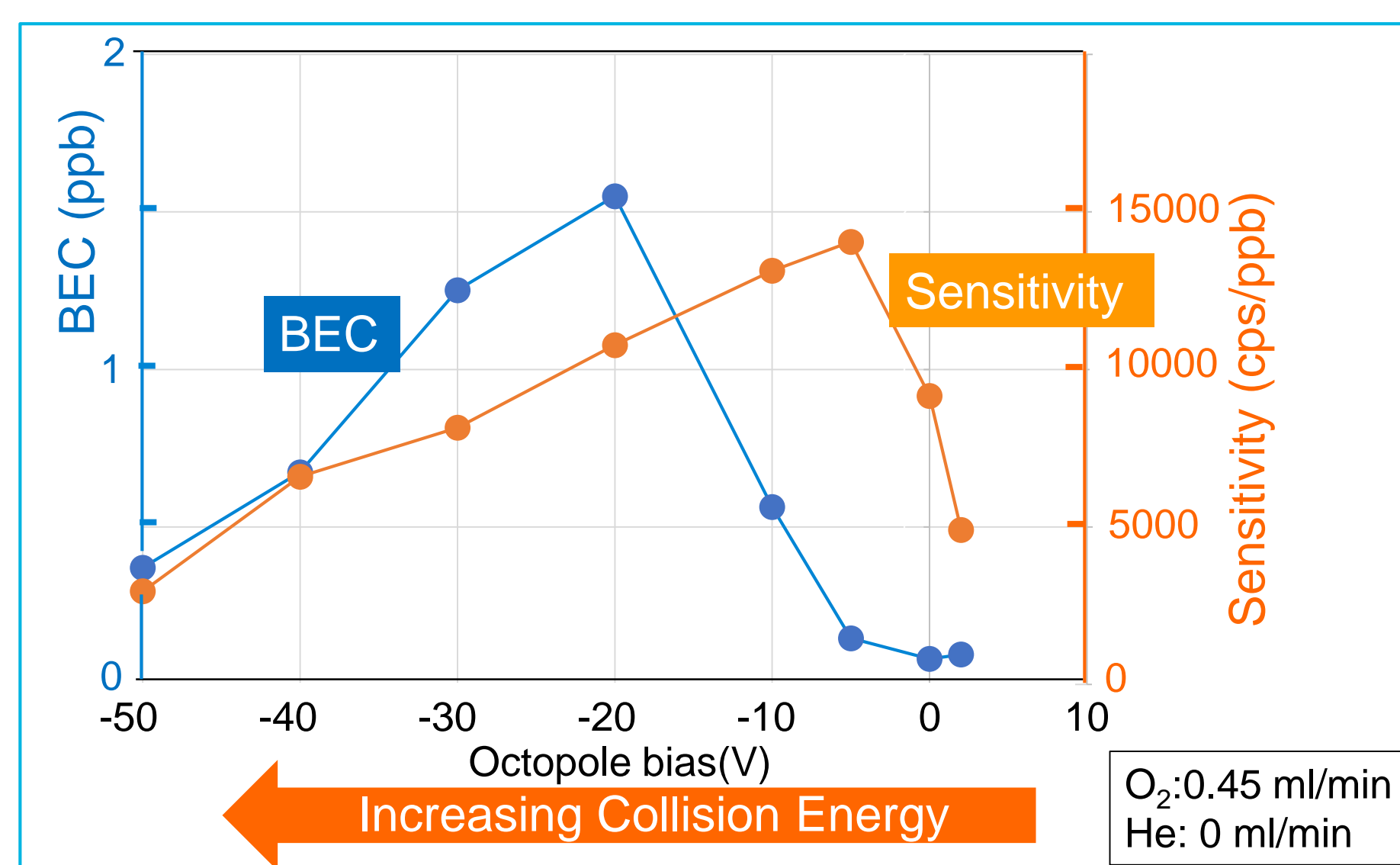


Figure 3 BEC vs Octopole bias in IPA

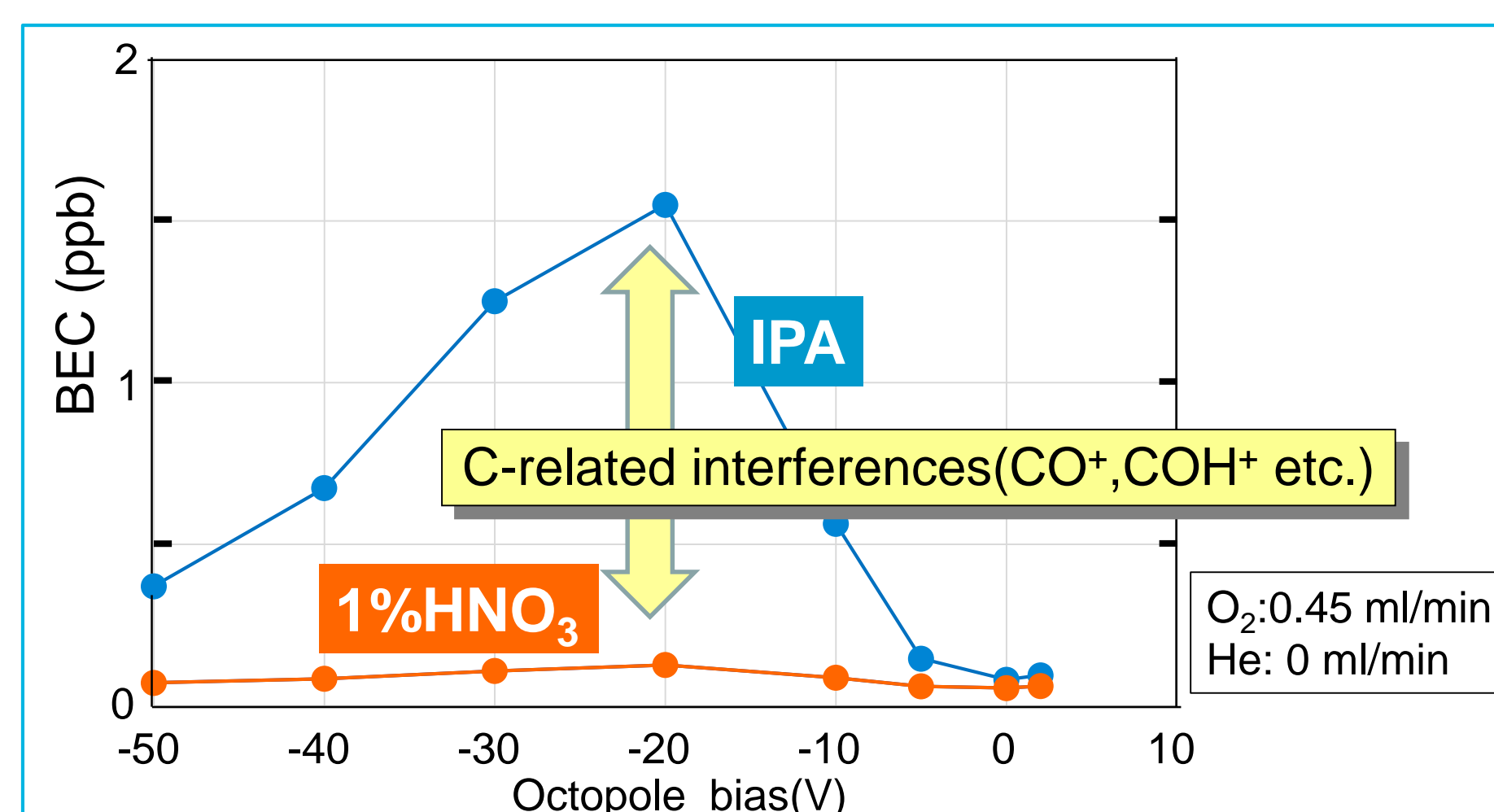


Figure 4 BEC vs Octopole bias. Comparison between IPA and 1% HNO<sub>3</sub>

From these results the cell conditions that give low collision energy are preferred due to the lower interfering product ions at *m/z* = 47 formed in the cell from C-based polyatomic ions at *m/z* = 31 (for example, <sup>13</sup>C<sup>18</sup>O<sup>+</sup> + O<sub>2</sub> → <sup>13</sup>C<sup>18</sup>O<sup>16</sup>O<sup>+</sup> + O). In general reaction rates are energy-dependent. Although not all the reactions involved here can be identified, it was found that low collision energy suppresses in-cell reactions that would otherwise produce ions that overlap <sup>31</sup>P<sup>16</sup>O<sup>+</sup>. To achieve low collision energy, a relatively high Octopole bias (-5V) was used together with a mixed cell gases of 0.075 mL/min oxygen plus 12 mL/min helium. Because the density of helium atoms in the cell is 160 times greater (12/0.075) than that of oxygen, most of the ions entering the cell undergo multiple collisions with helium before they collide with oxygen (see Fig.5). Thus, helium works as a buffer gas, reducing the kinetic energy of the ions before they react with the O<sub>2</sub> cell gas. Using these conditions a minimum BEC for P of 0.027 ppb (6666 cps/ppb) was obtained[2].

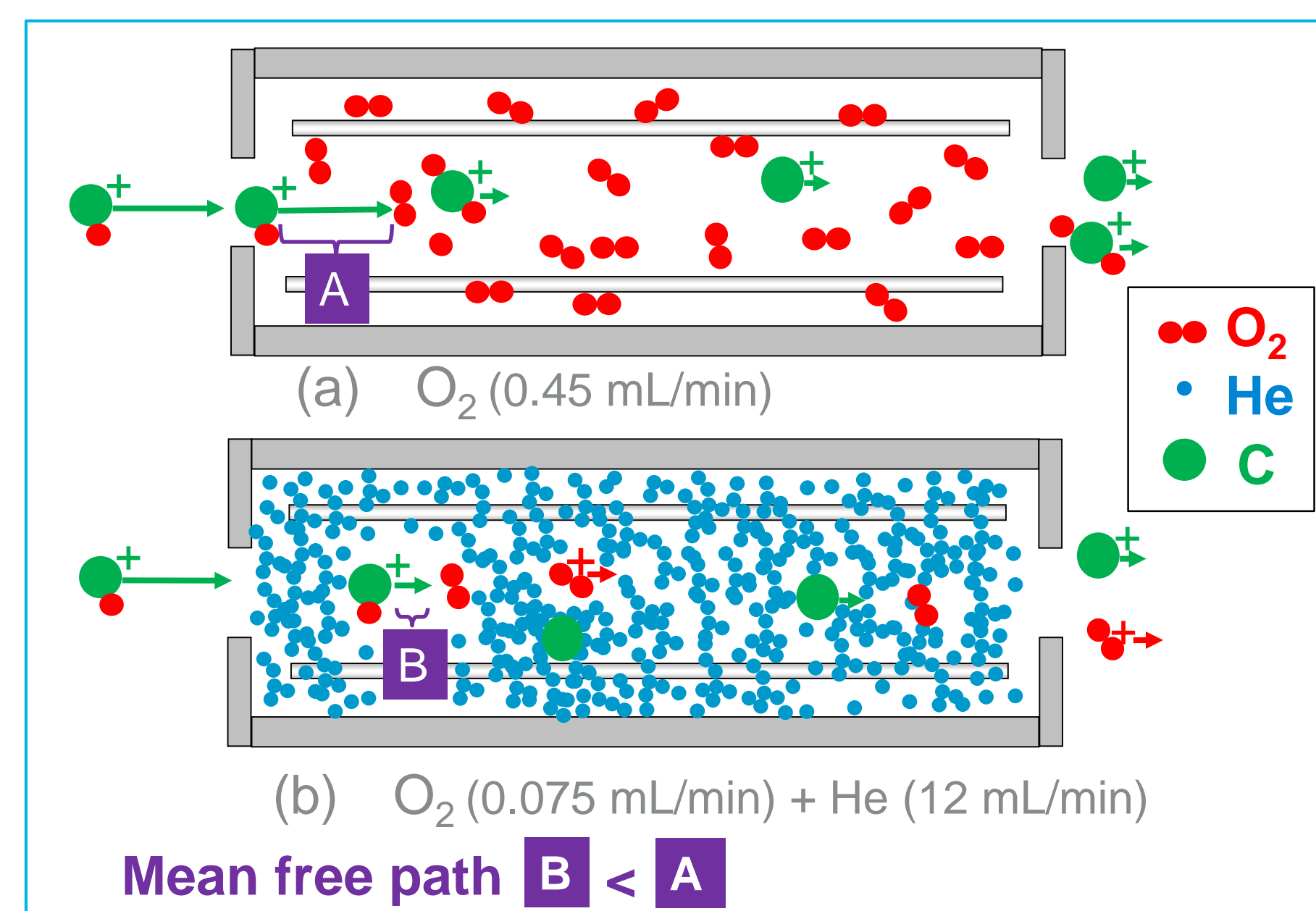


Figure 5 Collision process difference between O<sub>2</sub> mode with/without He addition in the cell

### (2) Hydrogen mass-shift (P as PH<sub>3</sub>/PH<sub>4</sub>)

Secondly, hydrogen mode (P detection as PH<sub>3</sub><sup>+</sup> and PH<sub>4</sub><sup>+</sup>) was investigated. In contrast to the exothermic O-atom transfer reaction (P<sup>+</sup> → PO<sup>+</sup>) as shown in Fig.1, the hydrogen transfer reaction (P<sup>+</sup> → PH<sup>+</sup> → PH<sub>2</sub><sup>+</sup> → PH<sub>3</sub><sup>+</sup>) is endothermic in each step (Fig.6). Fig.7 shows the sensitivity (a) and the BEC (b) for P (as PH<sup>+</sup>, PH<sub>2</sub><sup>+</sup>, PH<sub>3</sub><sup>+</sup>, PH<sub>4</sub><sup>+</sup>) in IPA as a function of Octopole bias. PH<sub>5</sub><sup>+</sup> was not produced in the range of Octopole bias investigated. The BEC for PH<sup>+</sup> was highest (worst) although the sensitivity was the highest (best). The BECs for PH<sub>3</sub><sup>+</sup> and PH<sub>4</sub><sup>+</sup> were less than 0.1 ppb. The BEC for PH<sub>4</sub><sup>+</sup> was the lowest, and it is almost independent of the Octopole bias. Using hydrogen transfer reaction (P<sup>+</sup> → PH<sub>4</sub><sup>+</sup>), the maximum sensitivity of 1150 cps/ppb for PH<sub>4</sub><sup>+</sup> was obtained at -30 V, which gave the lowest BEC of 0.021 ppb.

## Results and Discussion

The probable reaction pathway that leads to PH<sub>3</sub><sup>+</sup> and PH<sub>4</sub><sup>+</sup> is:

- P<sup>+</sup> + H<sub>2</sub> → PH<sup>+</sup> + H (Δ*H* = +1.13 eV[1]; endothermic);
- PH<sup>+</sup> + H<sub>2</sub> → PH<sub>2</sub><sup>+</sup> (Δ*H* < -2.69 eV[1]; association reaction);
- PH<sub>2</sub><sup>+</sup> + H<sub>2</sub> → PH<sub>3</sub><sup>+</sup> + H (Δ*H* = +0.05 eV[1]; negligibly endothermic).

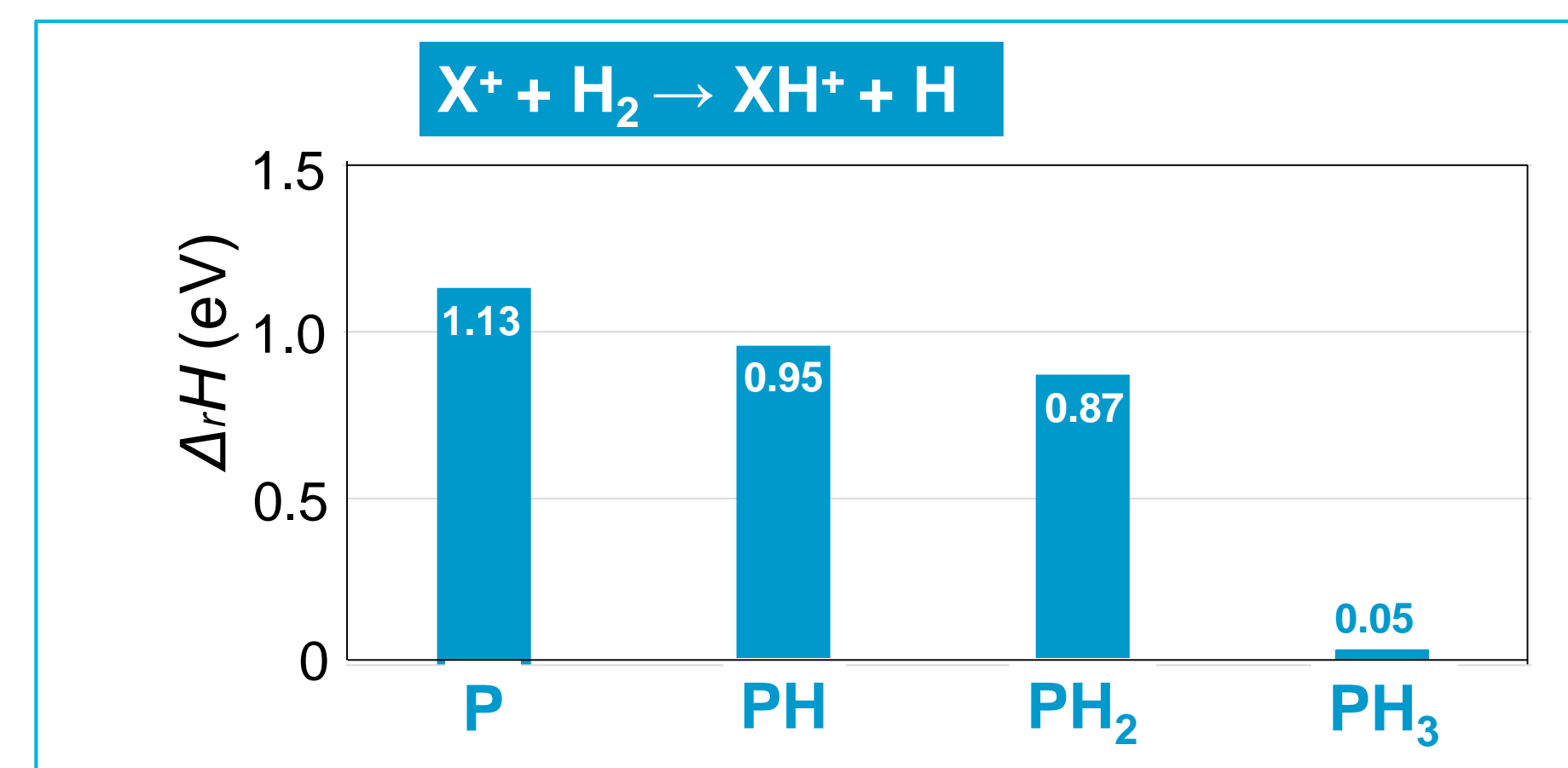
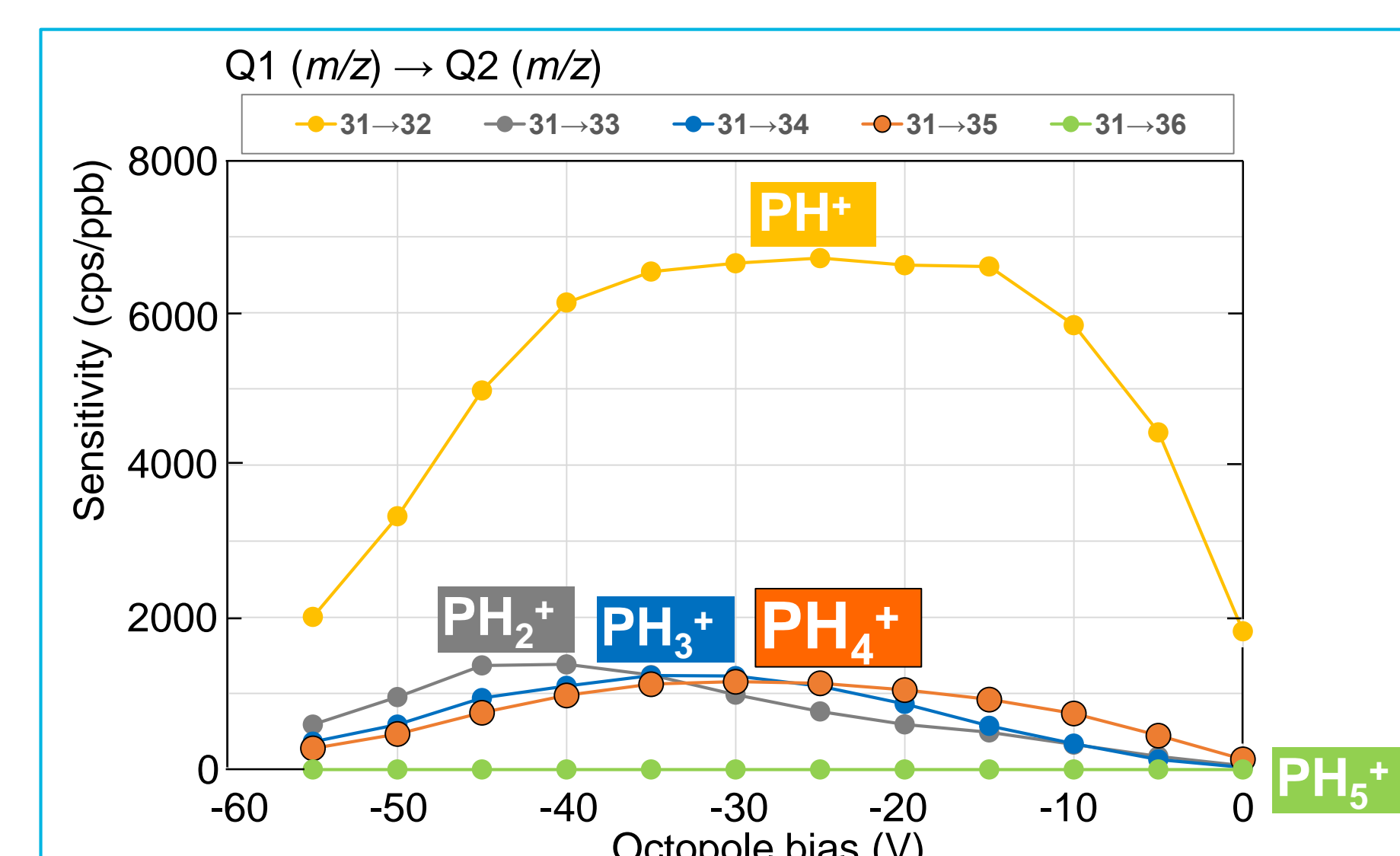
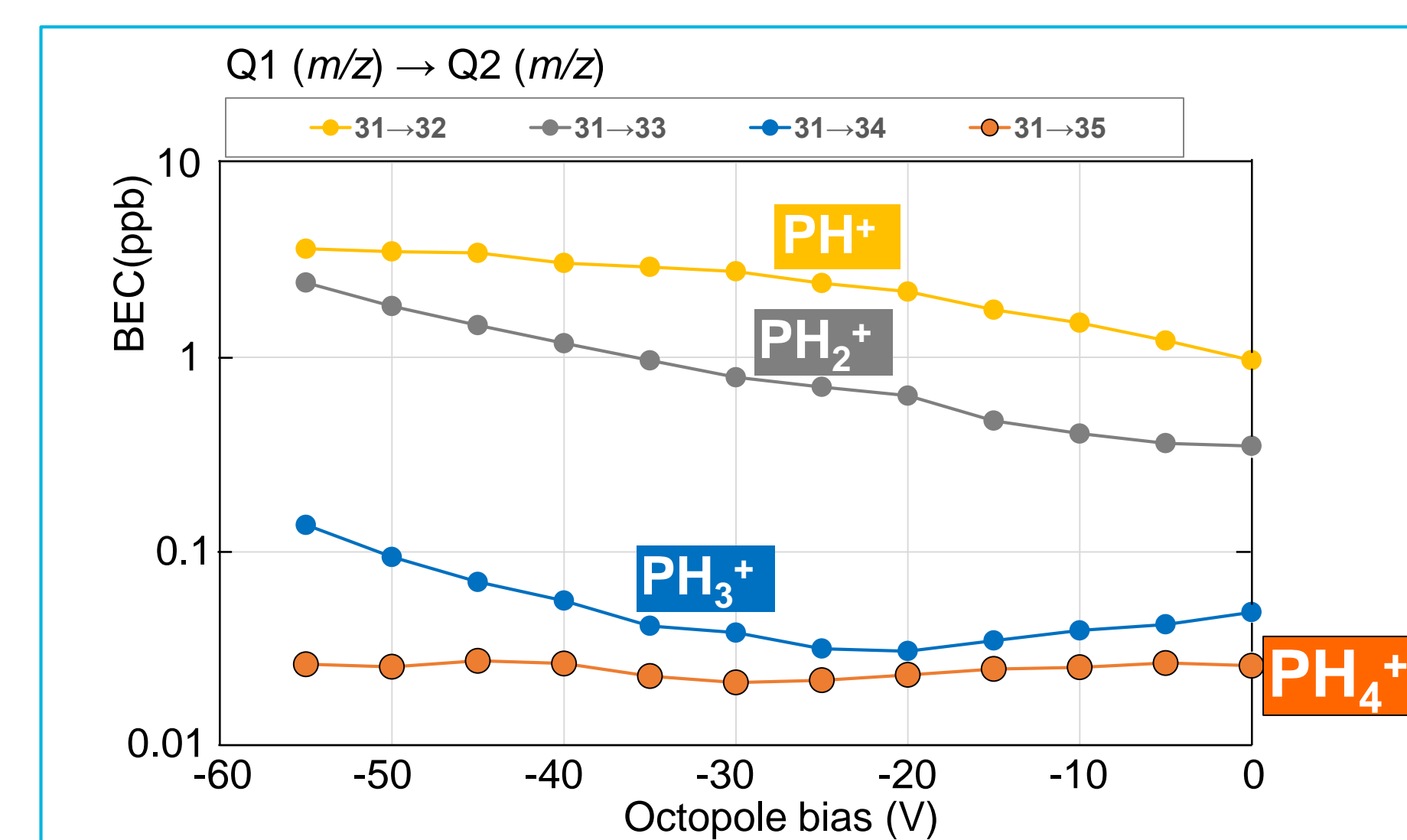


Fig. 6 Δ*H* for hydrogen transfer reaction of P<sup>+</sup>, PH<sup>+</sup>, PH<sub>2</sub><sup>+</sup> and PH<sub>3</sub><sup>+</sup> [1]

For efficient production of PH<sub>3</sub><sup>+</sup> and PH<sub>4</sub><sup>+</sup>, high collision energy is therefore required to promote the first endothermic reaction. This hypothesis is supported by Fig.7 (a) where the optimum Octopole bias (ca -30 V) is significantly lower than the O<sub>2</sub> mode that produces PO<sup>+</sup> exothermically.



(a) Sensitivity



(b) BEC

Fig. 7 Sensitivity (a) and BEC (b) vs OctP bias for P (as PH<sub>x</sub>) in IPA. H<sub>2</sub>: 10 ml/min (He: 0 ml/min)

## Conclusions

Two different reaction modes using MS/MS mode were studied to obtain the lowest possible BEC for <sup>31</sup>P in IPA, and the results were summarized in Table.2.

Table. 2 Summary for <sup>31</sup>P in IPA by Agilent 8900

	Q1→Q2	O <sub>2</sub>	He	H <sub>2</sub>	Octopole Bias	BEC	Sensitivity
	<i>m/z</i>	mL/min	mL/min	mL/min	V	ppb	cps/ppb
O <sub>2</sub>	31→47	0.45	0	0	0	0.082	9150
O <sub>2</sub> +He	31→47	0.075	12	0	-5	0.027	6660
H <sub>2</sub>	31→34	0	0	10	-30	0.038	1220
H <sub>2</sub>	31→35	0	0	10	-30	0.021	1150
He (ref)	31→31	0	5	0	-18	800	56

- The lowest BECs obtained for <sup>31</sup>P in IPA were:
  - 0.027 ppb by O<sub>2</sub> + He mode (P<sup>+</sup> → PO<sup>+</sup>) and
  - 0.021 ppb by H<sub>2</sub> mode (P<sup>+</sup> → PH<sub>4</sub><sup>+</sup>)
- For sensitivity, O<sub>2</sub> + He mode was superior to H<sub>2</sub> mode (about 6 times higher sensitivity).
- Compared to the conventional He mode ("He (ref)" shown in Table 2) reaction mode utilizing mass shift methods by ICP-QQQ with MS/MS result in drastic improvement for P analysis in IPA
- The BEC for P using the 8900 ICP-MS/MS was more than 4 orders of magnitude lower than the level of 800 ppb obtained in He mode. In addition the sensitivity was also increased by more than one order of magnitude.

## References

- [1] Journal of Physical and Chemical Reference Data, Vol 17,1988 Supplement No.1
- [2] K. Mizobuchi, N. Yamada and M. Yukinari, The Japan Society for Analytical Chemistry, 2017 66th Nenkai, G4002