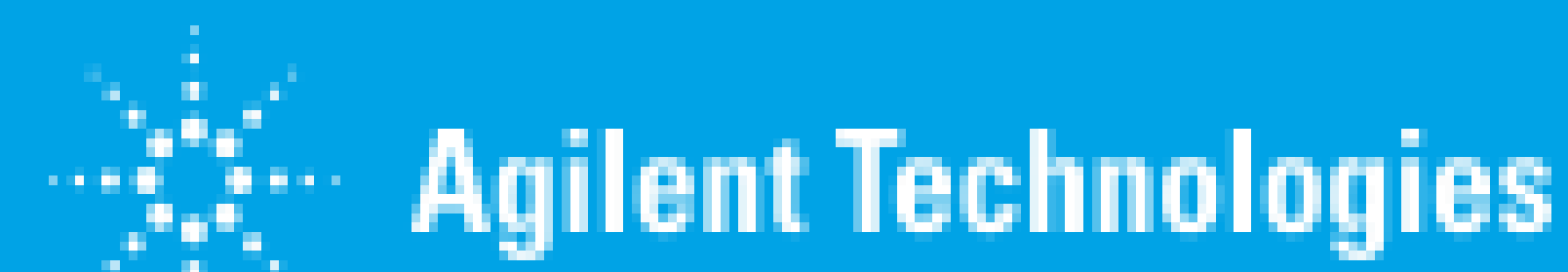


Analysis of radioactive iodine-129 by ICP-QQQ using MS/MS mode and a new octopole reaction cell with axial acceleration

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Introduction

Since the explosion at the Fukushima Daiichi Nuclear Power Plant (FDNPP) resulting from the tsunami in 2011, determination of radionuclides in various samples has been of great interest. Especially important is the analysis of long-lived radionuclides such as iodine-129 (¹²⁹I; T_{1/2} = 1.57 × 10⁷ y) which are measured to investigate the diffusion of radionuclides from the FDNPP, and to study the mechanism of the explosion that occurred at the nuclear reactor.

Isotopic analysis of ¹²⁹I/¹²⁷I is challenging because of the enormous signal abundance difference (more than 10⁷) between ¹²⁷I and ¹²⁹I, both of which must be measured to give a ratio.

In previous work¹⁾, an Agilent 8800 ICP-QQQ with oxygen (O₂) as the reaction cell gas was used to investigate the possible interference on ¹²⁹I from ¹²⁷IH₂. The results indicated that both ¹²⁷ID and ¹²⁷IH₂ polyatomic ions occur at a level that impacts significantly on the measurement of I at m/z = 129. Consequently, blank subtraction of total ¹²⁷ID and ¹²⁷IH₂ needs to be applied to enable low-level determination of ¹²⁹I.

When a relatively heavy reaction cell gas such as oxygen is used, the ions passing through the cell lose a lot of energy due to multiple collision with cell gas molecules.

As well as causing a significant reduction in analyte sensitivity, the energy loss causes ions to decelerate in the cell,

In the current work, we used the 2nd generation ICP-QQQ, the Agilent 8900, incorporating a new octopole reaction cell with axial acceleration. In addition to increasing the transmission and therefore sensitivity of low-energy product ions, axial acceleration also improves discrimination of slow-moving ions that can cause interferences due to artifact signals at the target analyte mass, especially with a relatively heavy cell gas such as O₂. The 8900 provides a solution to improve sensitivity by allowing an axial acceleration voltage to be applied to the octopole rods. By applying an electric potential gradient in the axial direction, the ions that have been decelerated by collision with the O₂ cell gas molecules can be accelerated again, correcting the loss of sensitivity. The newly developed Octopole cell is shown in Figure 1.

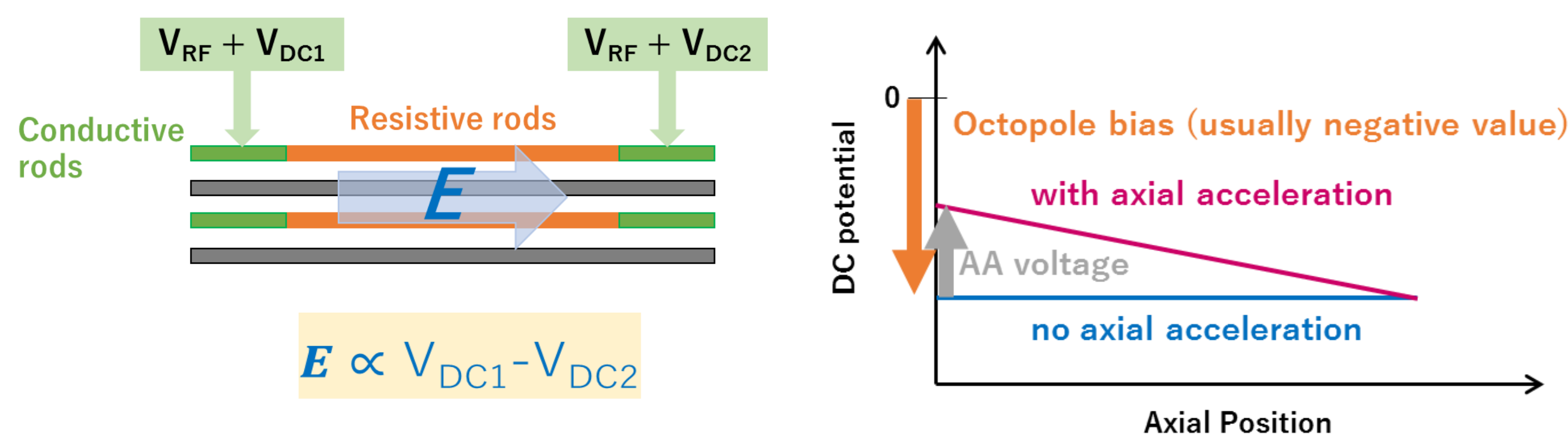


Figure 1 Octopole schematic and potential diagram of Axial Acceleration

In this study, we used ICP-MS/MS with axial acceleration to study the effect of IH₂ and ID interferences on radioactive iodide ¹²⁹I in more detail. Using ICP-QQQ with O₂ reaction cell gas mode and axial acceleration or deceleration, our results show a significant improvement in the measurable ratio of ¹²⁹I/¹²⁷I by in-cell energy discrimination with retarding axial field.

Experimental

Instrumentation : ICP-QQQ with MS/MS (Agilent 8900 Triple Quadrupole ICP-MS #100)

Instrumental conditions:

Preset Plasma : Low matrix conditions (RF 1550W, Sampling depth 8mm, Carrier gas flow rate 1.05L/min)

Ion Lens tune : Extract 1 = 0V, Extract 2 = -190V.

ORS and acquisition parameters : O₂ 0.7mL/min, He 2mL/min

Axial acceleration or deceleration : -2V to 2V

Sample preparation

I-127 stock solution ; Potassium Iodide (analytical grade; Kanto Chemical Co. Inc., Tokyo, Japan) was dissolved in deionized water.

Results and Discussion

Effect of applied axial acceleration (+ve AA voltage) and deceleration (-ve AA voltage) on the signal at m/z 127 (I-127) and 129 (O₂ reaction mode)

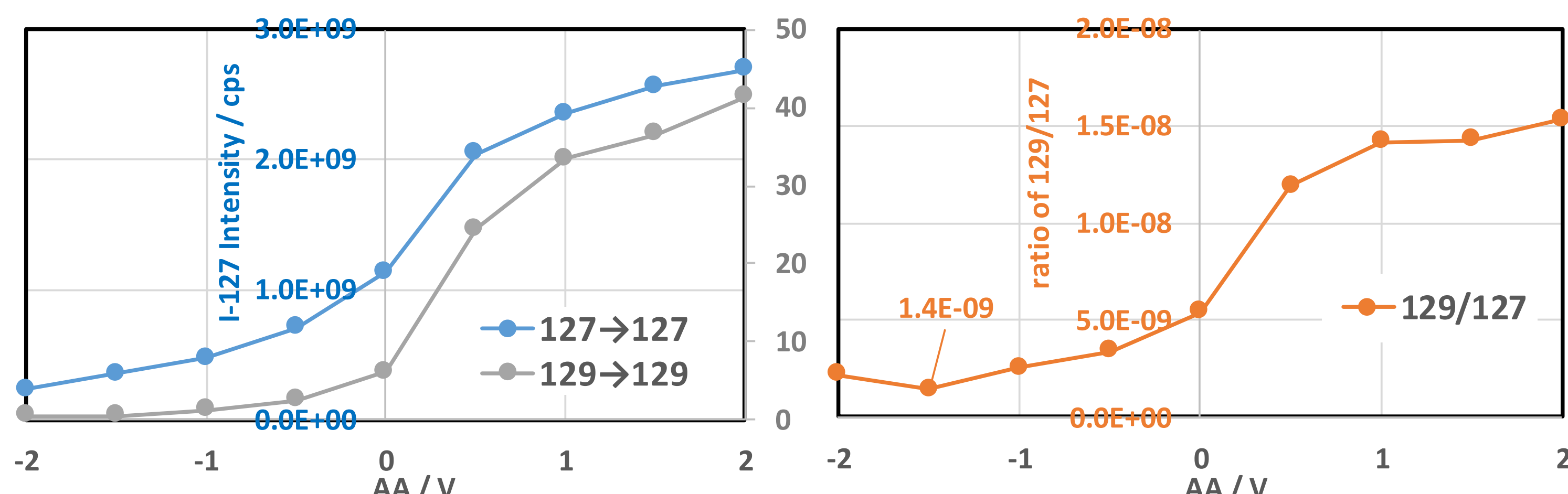


Figure 2 Signal change of ¹²⁷I & ¹²⁹I(bkg) (left), and ¹²⁹I(bkg)/¹²⁷I (right) vs acceleration voltage.

Compared to the condition of 0 V AA voltage, the signal intensity of ¹²⁷I was increased by X2.5 with an accelerating AA voltage of +2 V. The background signal at m/z 129 also increased with increasing positive axial acceleration voltage. The contribution from I-127 to the signal at m/z 129 (ratio of I-129/I-127) increased from 5 × 10⁻⁹ to 1.5 × 10⁻⁸ with axial acceleration. This may be due to the effective “competition” between AA voltage and KED, which would normally reduce the transmission of polyatomic species of I-127.

Reaction of I⁺ and MS/MS setting (O₂ reaction mode)

There may also be a contribution from an endothermic reaction leading to an increase in the background signal from product ions formed in the cell. Production process of IH⁺, IH₂⁺, ID⁺ and MS/MS settings are shown below.

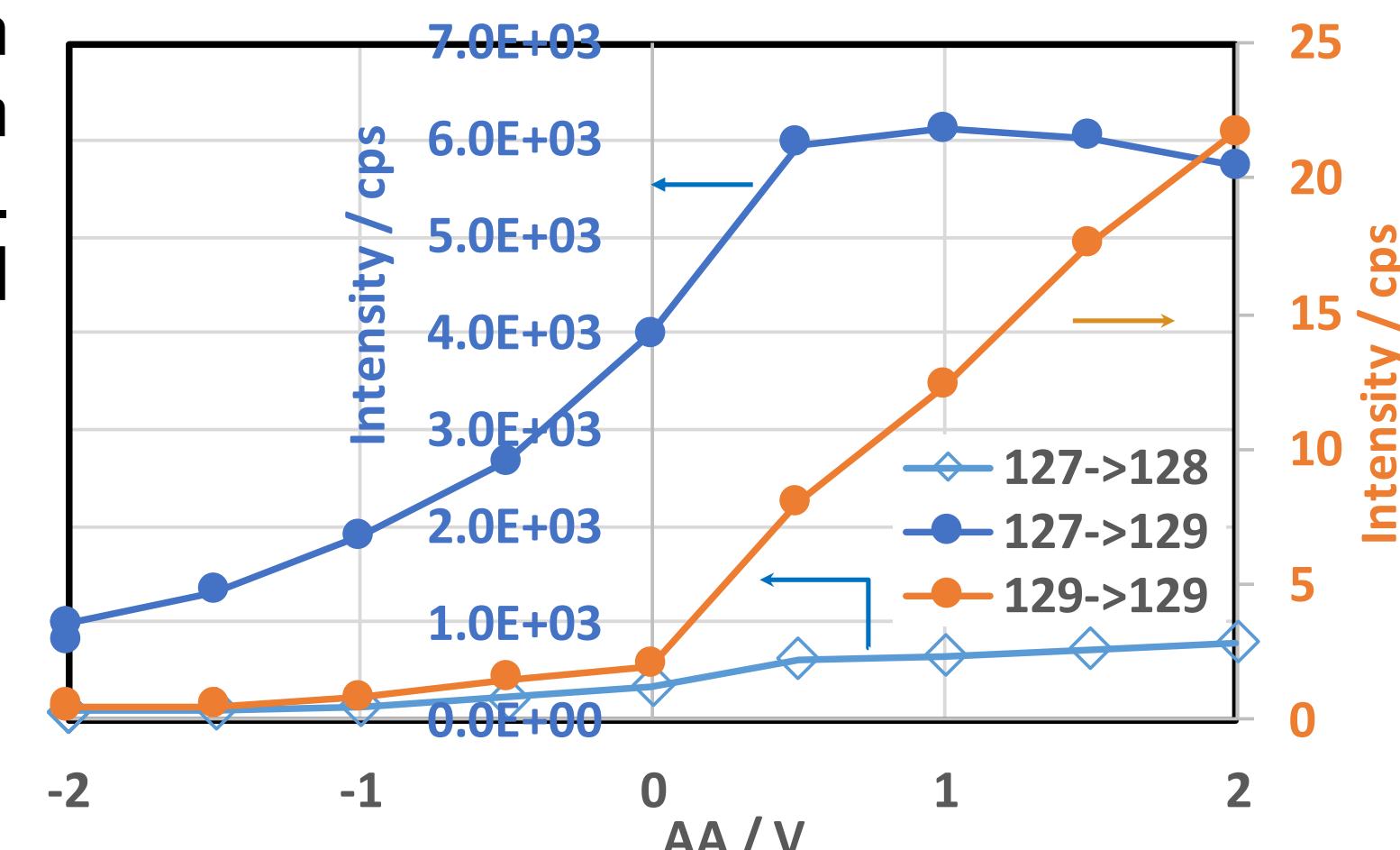
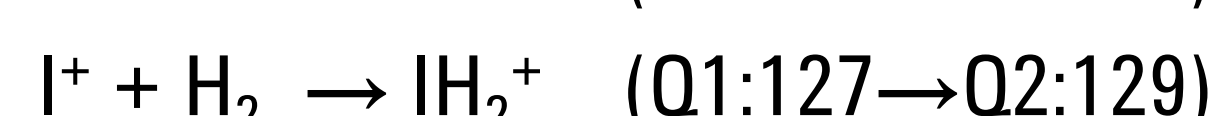
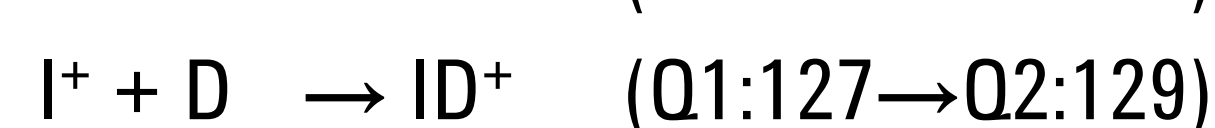
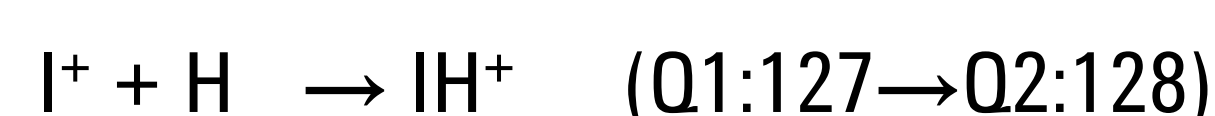


Figure 3 IH⁺, IH₂⁺ signal change vs axial acceleration voltage

In-cell production of IH⁺ and IH₂⁺ was confirmed by introducing 100 ppm I-127 solution, as shown in Figure 3. Increasing the AA voltage appears to promote the generation of these hydride ions. IH₂⁺ signal produced was around ten times higher than that of IH⁺, although neither of these polyatomics would give a significant signal under normal MS/MS conditions with Q1 at m/z 129.

Signal change of ¹²⁷I, ¹²⁹I (bkg) for the applied axial acceleration (AA) voltage in the octopole reaction cell by adding He gas as cell gas (O₂+He mode)

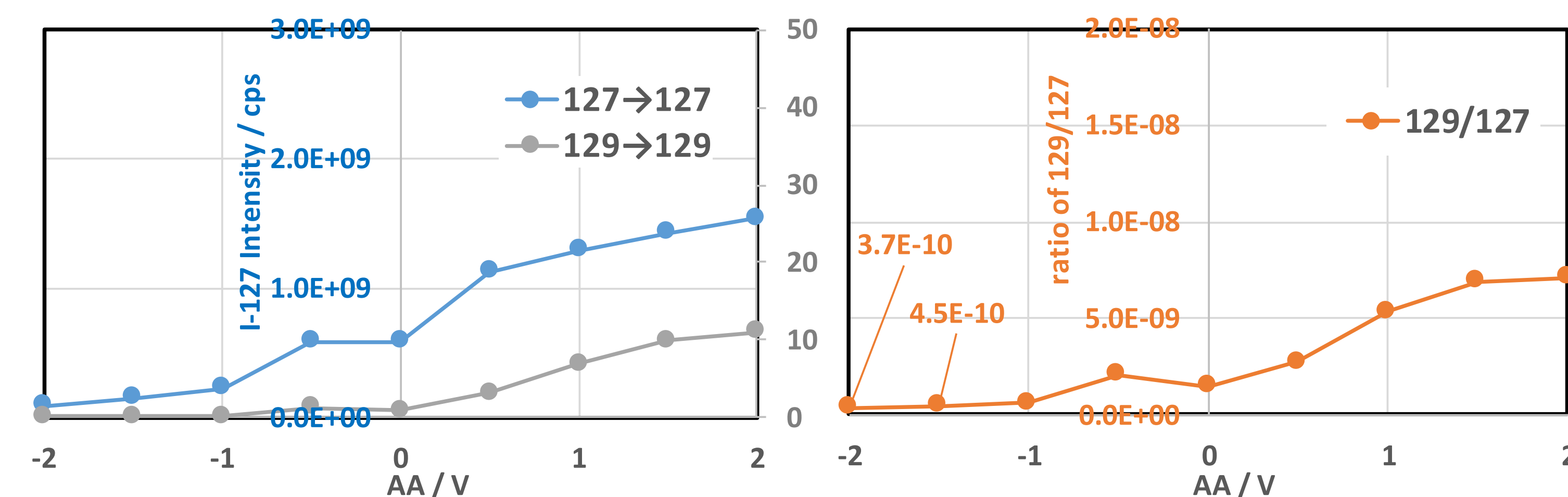


Figure 4 Signal ¹²⁷I, ¹²⁹I(bkg) (left) and ¹²⁹I(bkg)/¹²⁷I (right) vs axial acceleration voltage.

As with the data shown in Figure 2, both ¹²⁷I and ¹²⁹I(bkg) increased with a more positive axial acceleration voltage. As a result, ¹²⁹I(bkg)/¹²⁷I was increased and the superior transmission of I-127 polyatomic ions through the cell was assumed. He gas was added (He and O₂ cell gas) in order to attenuate such ions by energy discrimination, and to suppress the formation of cell-formed product ions. The m/z 129 background was further reduced by applying a negative axial acceleration voltage, enabling a ¹²⁹I(bkg)/¹²⁷I ratio at the 10⁻¹⁰ level to be achieved.

Conclusions

- By applying a positive axial acceleration voltage in an octopole reaction cell, the sensitivity of ¹²⁷I⁺ was increased by approximately X2.5, compared with no acceleration.
- However, the generation and/or transmission of I-based polyatomic ions (IH⁺, IH₂⁺) was also promoted.
- Axial **deceleration** (negative AA voltage) and the addition of He cell gas was successful in reducing the background signal at m/z 129.
- The ratio of I-129/I-127 was decreased to the 10⁻¹⁰ level for a sample of 100 ppm I. This background level is an improvement of approximately two orders of magnitude compared with the ratio of 1.3 × 10⁻⁸ obtained on Agilent 8800 without axial acceleration (reference 2).

References

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