Arsenic(As) and Selenium(Se) analysis in presence of Rare Earth Elements (REEs) by single quadrupole ICP-MS

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Introduction

Helium (He) Kinetic Energy Discrimination (KED) is a widely used technique to resolve spectra interference of ICP-MS. He KED is , however ineffective against doubly charge ion (M^{++}) overlap. In general, interference by M^{++} is not a big issue though, there are cases where doubly charged ion of rare earth elements (REEs) interfere with As and Se; $^{75}As^{+}$ suffers from overlap by $^{150}Nd^{++}$ and $^{150}Sm^{++}$, and $^{78}Se^{+}$ from $^{156}Gd^{++}$ and $^{156}Dy^{++}$. This reports a method to measure trace As and Se in presence of REEs by single quadrupole ICP-MS (ICP-SQ).

Figure 1-1 is a stopping curve of singly charged ion (M^{+}) and doubly charged ion (M^{++}) of same isotope, neodymium (Nd) in He cell. It indicates M^{++} and M^{+} has almost same collision cross section area to He molecule, suggesting that He KED cannot attenuate M^{++} . As shown in Figure 4 , BEC of As and Se in presence of REE is worse in He KED than in Nogas , because lighter As^{+} and Se^{+} lose more Kinetic Energy (KE) than heavier REE^{++} with every collision.

Figure 1-2 is a stopping curve of Nd^{+} and Nd^{++} in Hydrogen (H2) cell, showing that M^{++} drops more rapidly than M^{+} . It indicates M^{++} has larger cross section area than M^{+} to H_2 molecule. It is a typical ion-molecule interaction via induced dipole due to the large polarizability of H_2 molecule. Based on the finding, H_2 was studied to attenuate REE^{++} interference on As^{+} and Se^{+}.

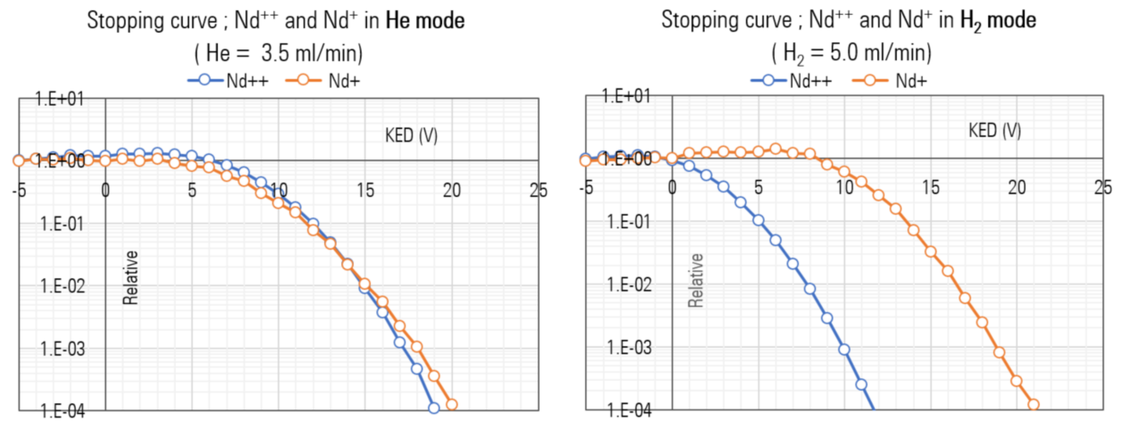

Figure 1 Stopping curve of Nd^{++} and Nd^{+} at octpoleBias = -18V. Signal of the ions , given in normalized signal was measured as a function of KED. KED is a difference between quadrupole bias voltage and octpole ion-guide bias voltage.
Figure 1-1 (left) stopping curve in He cell and Figure 1-2 (right) stopping curve in H_2 cell.

Experimental 1 : H_2 KED mode 1) typical tune

Figure 4 gives BEC of As and Se in presence of REE in H_2 KED using typical tuning conditions summarized in table1. While BEC of Se was dramatically improved as expected, BEC of As was Not.

This is because As^{+} is a unique singly charged ion having large collision cross section area to H_2. Figure 2 shows signal suppression of elemental ions in H_2 KED mode. Some element such as Ni, Cu and As shows significant suppression, which suggests they have large cross section area to H_2.

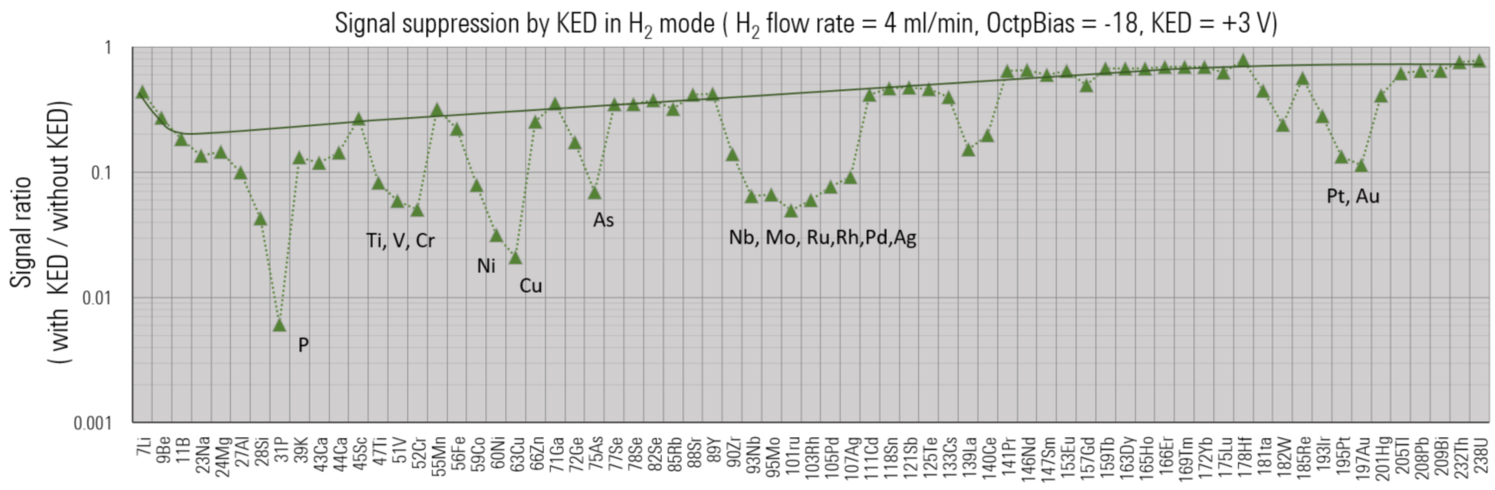

Figure 2 Signal suppression in H_2 KED. Signal ratio (with KED /without KED) is given to each element. Small ratio indicates that the elemental ion has large collision cross section area toward H_2 molecule.

Experimental 2 : H2 KED mode 2) OctpBias = -6V

There are three tuning parameters which affect cell performance ; Cell gas flow rate, OctpBias and KED. I found that high OctPBias (-6V) attenuated REE^{++} interference on As^{+}. As shown in Figure 4, BEC < 0.5ppb was achieved for As and Se in presence of 1ppm REE with the condition. Applying common interference mathematical correction to data further reduced the BEC , below 50ppt.

Measured stopping curve of As^{+} and Nd^{++} was given in Figure 3 for two H_2 KED conditions. With OctpBias = -6V, the cross section area of Nd^{++} gets larger (signal drops faster with KED) to H_2. It improves the BEC of As to satisfactory level at sacrifice of sensitivity. However, with integration time of 3s , MDL < 30ppt (0.1ppb x n = 9) was achieve for both As and Se.

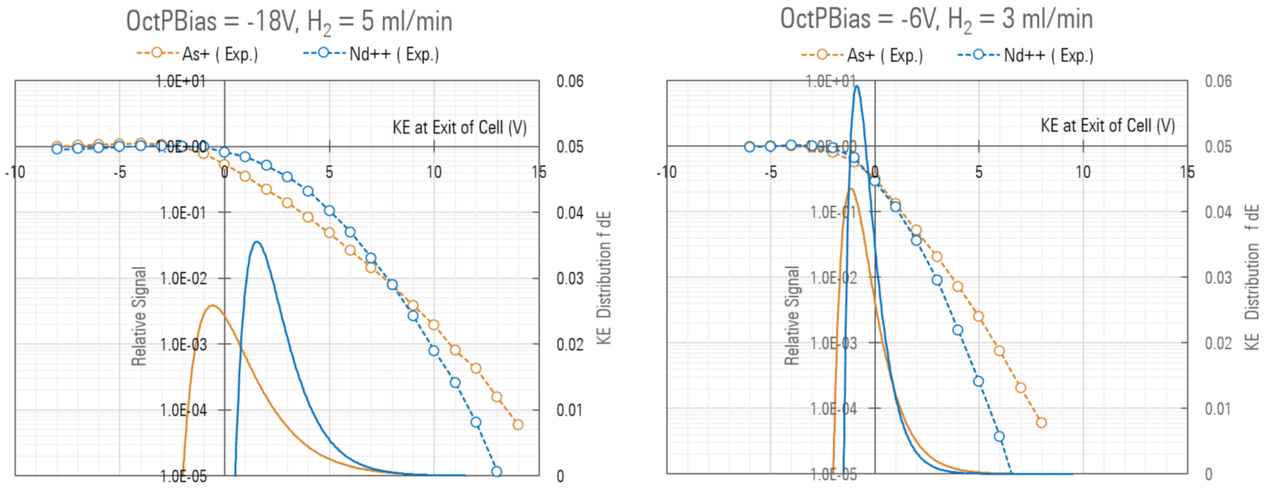

Figure 3 Stopping curve of As^{+} and Nd^{++} in two H_2 conditions. Figure 3-1 (left) H2 1) typical tuning and Figure 3-2 (right) H2 2) OctpBias = -6V. KE distribution of ions , calculated from the stopping curve are also given.

Result and Summary

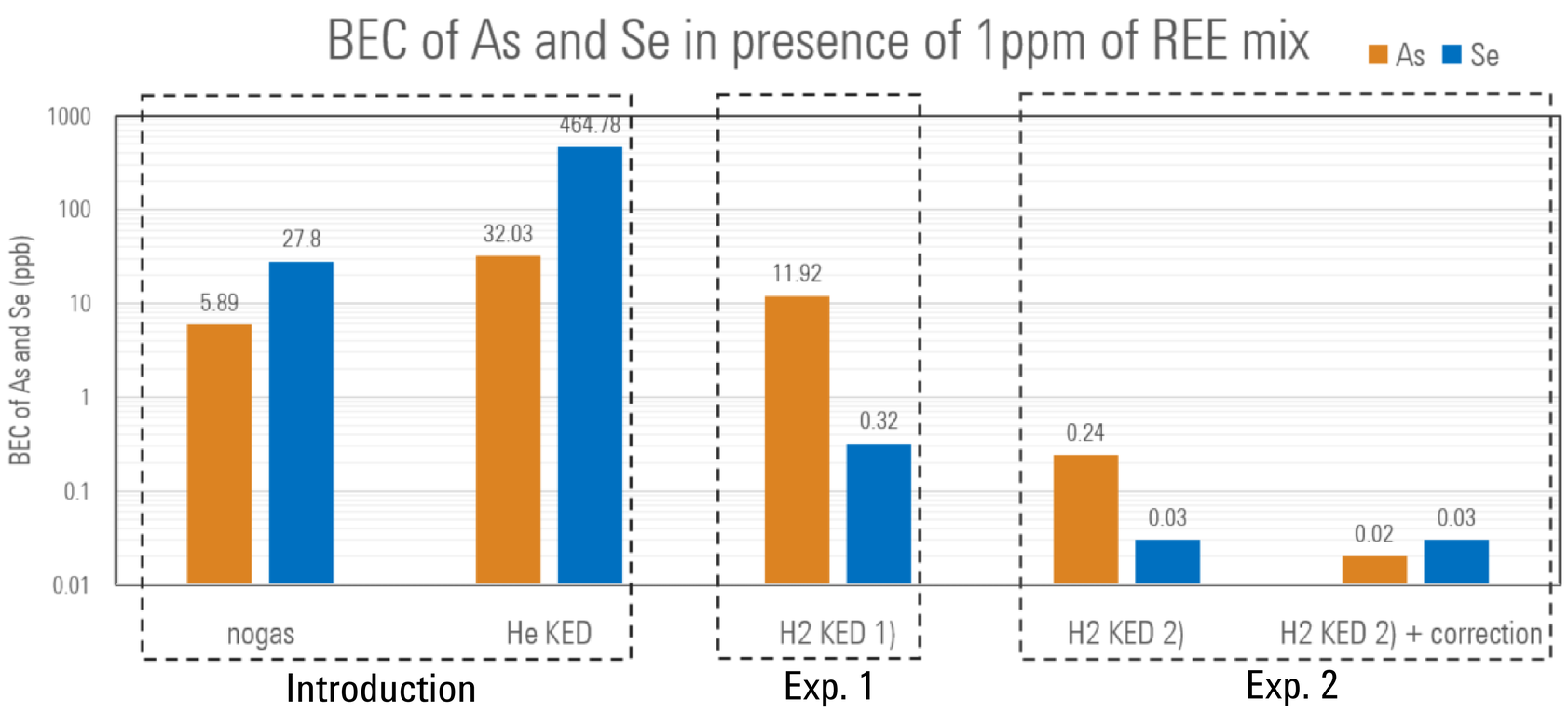

Figure 4 Summary of the study; BEC of As and Se in presence of 1ppm REE mixture (1ppm of each of Nd, Sm, Gd and Dy).

Table 1 : Tuning conditions
Instrument ; Agilent 7900 x-lens
Plasma condition ; General purpose Plasma

		Nogas	He KED	H_2 KED 1)	H_2 KED 2)
Cell gas		NA	He	H_2	H_2
Cell gas flow rate	ml/min	NA	4.5	6.0	3.0
octPbias	V	-5	-18	-18	-6
KED	V	3	3	3	4
Cell Exit	V	-50	-50	-50	-50
Deflect	V	15	-5	2	7
Plate Bias	V	-40	-50	-50	-20

Summary and Conclusions

- He KED cannot attenuate the REE^{++} interference on As and Se , since M^{++} has almost same collision cross section area as M^{+} to He .
- H_2 KED has more chance to resolve the interference, since M^{++} has larger cross section area than M^{+} to H_2 molecule.
- H_2 KED attenuated REE^{++} interference on Se^{+}, but didn't REE^{++} interference on As^{+}, since As^{+} uniquely has large cross section area to H_2.
- H_2 KED with OctpBias = -6V , attenuated the REE^{++} interference on As^{+}, allowing BEC < 0.5 ppb for As and Se in presence of 1ppm REEs.
- Use of common mathematical correction in the H_2 KED mode further lowered the BEC to 0.03 ppb for As and Se, allowing accurate determination of 1ppb As and Se in presence of 1ppm REEs.