PC-013 Enhancing Helium Mode Performance to Provide Improved Detection Limits for Difficult Elements Including S, P, Fe, and Se

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2011 European Winter Conference on Plasma Spectrochemistry, Zaragoza, Spain

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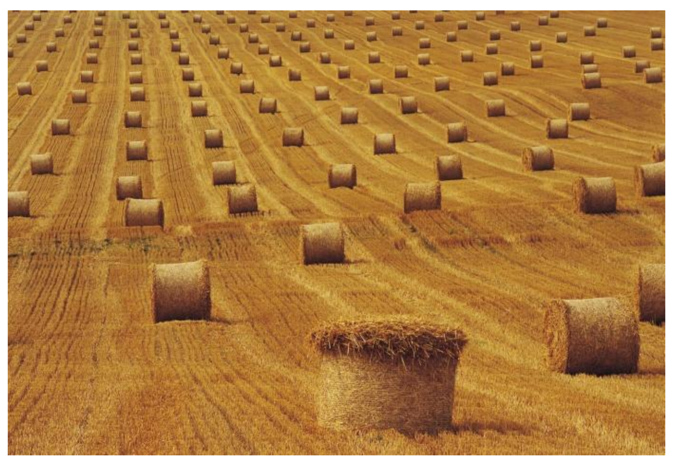
Abstract

Helium (He) Collision Mode with Kinetic Energy Discrimination (KED) is now widely acknowledged as the only reliable collision/reaction cell approach to remove multiple unknown interferences in the complex and variable sample types commonly found in many real-world applications. However, until recently He mode was unable to reduce some of the most intense background interferences effectively enough to allow low ng/L (ppt) detection limits for some of the typical regulated elements, notably Selenium. As a result, many analysts have had to retain a reaction cell gas method for those specific analytes, which impacts on the ease of operation of the method as well as the productivity, due to the extra time required to switch gas modes to provide the full analysis.

With the new collision/reaction cell design and operating conditions of the Agilent 7700 Series, the performance of He mode has been improved dramatically, with single-ppt detection limits now possible for Se in He mode. Several other previously difficult elements have also seen significant improvements in detection limits, allowing most routine applications other than high-purity chemical analysis to be carried out without requiring any reactive cell gases.

Introduction



Several elements such as P, S, As and Se have been difficult to analyze by conventional ICP-MS, due to their high ionization potential, low isotopic abundance, overlap from polyatomic interferences, or a combination of these.

Some elements, such as Se, suffer all these effects, leading to both low sensitivity and high background signal. Selenium analysis is further complicated by the fact that it is often required to be measured at extremely low (ng/L or ppt) concentrations. In addition, Se analysis frequently requires separation of the different chemical forms or "species" in which the Se is present, and this separation (usually by HPLC) further reduces the signal available for the measurement of each individual Se species.

The low sensitivity available for Se, combined with the presence of a background interference from Ar_2 ($^{38}Ar^{40}Ar$ on ^{78}Se and $^{40}Ar_2$ on ^{80}Se) mean that Se is one of the elements that has benefited most from the introduction of collision/reaction cells (CRCs) in ICP-MS. However, low-level (single ng/L or ppt) analysis of Se has previously only been possible with the use of a reactive cell gas. On Agilent's CRC instruments, H_2 cell gas has typically been used for the measurement of Se at low levels, but H_2 (in common with all other reaction gases) is not applicable to multi-element analysis or to the analysis of complex or unknown sample matrices, due to:

1. The loss of sensitivity for some analytes caused by reaction of the analyte ions with the cell gas
2. The unpredictable new interfering product ions formed from reactions between the cell gas and other analytes or matrix elements, and
3. The fact that each reaction gas can only remove certain reactive interferences, so each reaction gas must be targeted at selected known interferences in each sample.

Helium Mode and KED

For these reasons, He mode with Kinetic Energy Discrimination (KED) has become widely accepted as the most reliable and widely applicable mode for polyatomic interference removal, and the principles of operation of the Octopole Reaction System (ORS) used on the Agilent 7700 Series is shown in Figure 1.

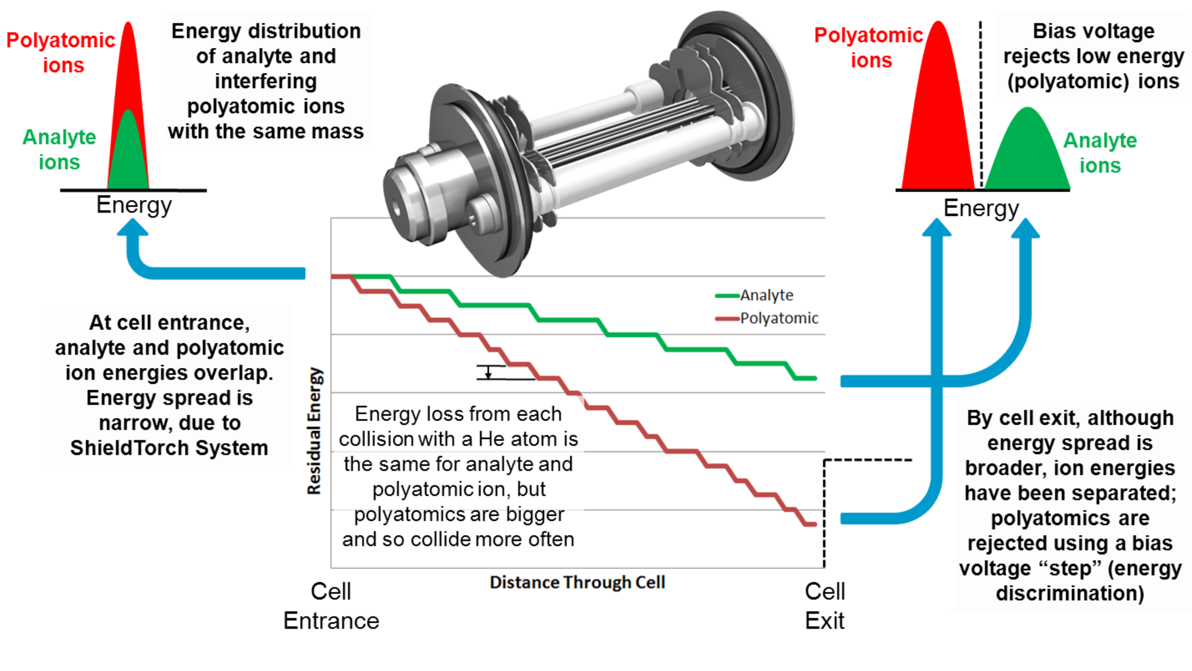


Figure 1. Schematic illustrating the principles of operation of He collision mode and interference removal using KED.

The effectiveness of He mode to reduce a wide range of polyatomic interferences is demonstrated in the spectra in Figure 2. These illustrate the complex background spectrum observed when a mixed matrix containing several common matrix elements is measured in no gas mode (top), compared to the same sample matrix measured in He mode (bottom).

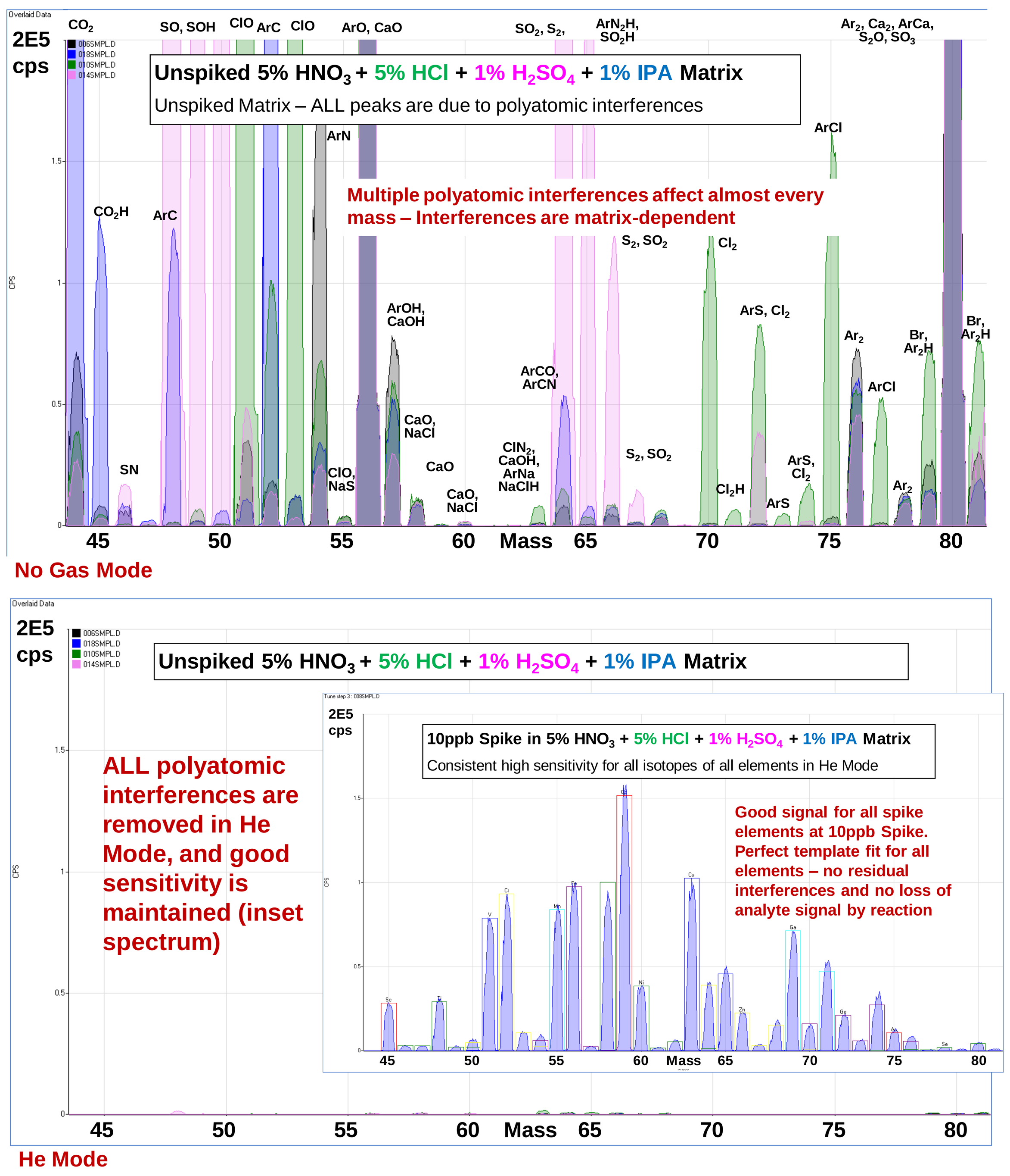


Figure 2. Comparison of background spectra for typical mixed matrix in no gas mode (top) and He mode (bottom). Inset spectrum shows spiked matrix (10ppb) in He mode

The spectrum comparison in Figure 2 demonstrates that conventional (ORS[2]) He mode can effectively reduce the Ar_2 interferences on Se, but the inset spectrum of the 10ppb spike also demonstrates that the residual sensitivity for Se is very low, so detection limits for Se are compromised (background equivalent concentration (BEC) of about 150ppt for ^{78}Se)

Results and Discussion

The performance of the new ORS[3] collision/reaction cell was evaluated for Se at mass 78. In addition to investigating whether He mode could effectively remove the Ar_2 polyatomic interference, the sensitivity for Se in the ORS[3] was evaluated compared to the previous ORS[2]. High analyte sensitivity depends on creating a large difference in the residual energy that the analyte and polyatomic ions retain after passing through the cell.

The upper plot in Figure 3 illustrates that the relatively low cell gas flow and low collision energy of the previous ORS[2] cell leads to a large overlap in the residual energy of the Se and Ar_2 ions after passing through the cell. This means that the bias voltage required to exclude the Ar_2 ions (typically ~5V) also leads to the rejection of a large proportion (more then 50%) of the Se ions.

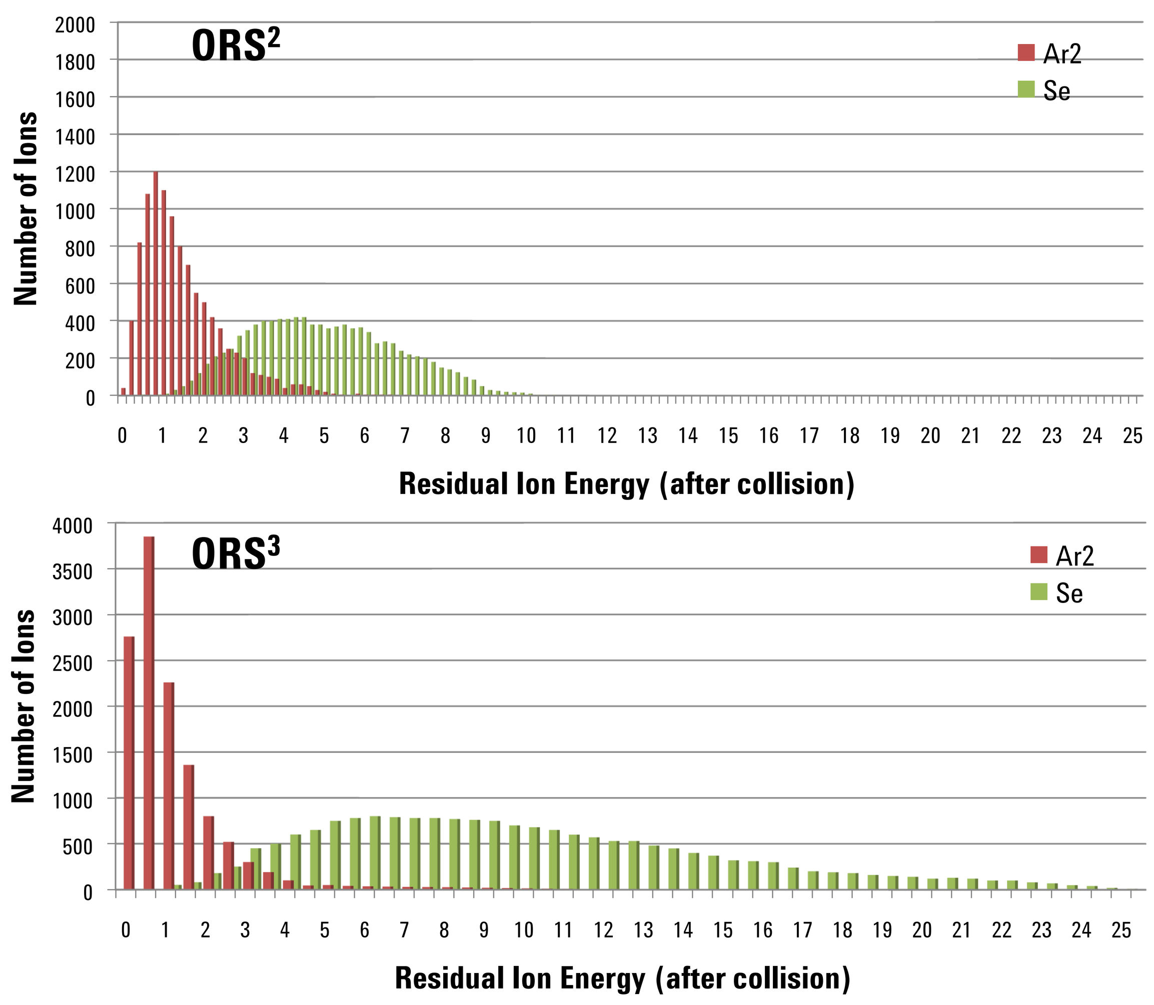


Figure 3. Residual (after the collision/reaction cell) energy profiles for Se and Ar_2 ions in ORS[2] (top) and ORS[3] (bottom)

The lower plot in Figure 3 shows the residual ion energy profiles for Se and Ar_2 in the ORS[3]. The higher collision energy used in the ORS[3] gives improved separation of the Se and Ar_2 ions, so that the 5V bias voltage required to exclude the Ar_2 ions rejects less than 10% of the Se ions. This leads to an improvement in sensitivity and detection limit of about a factor of 10 compared to the ORS[2] performance. Furthermore, the higher ion energy allows a higher cell gas flow rate to be used, which further improves separation of the Se and Ar_2 while maintaining analyte sensitivity.

Collision Induced Dissociation

Collision Induced Dissociation (CID) occurs when the collision energy is greater than the bond energy of the polyatomic ion. In the case of Ar_2, which has a bond energy of 1.33eV, CID does not occur under ORS[2] collision conditions, where the center-of-mass collision energy of Ar_2 with He is only 0.98eV. In the ORS[3] however, the collision energy is much higher at 4.88eV, easily enough to promote CID of the Ar_2 polyatomic. The effect of CID is evident from the cell gas optimization plot shown in Figure 4, where the initial rapid reduction in Ar_2 signal is due to CID.

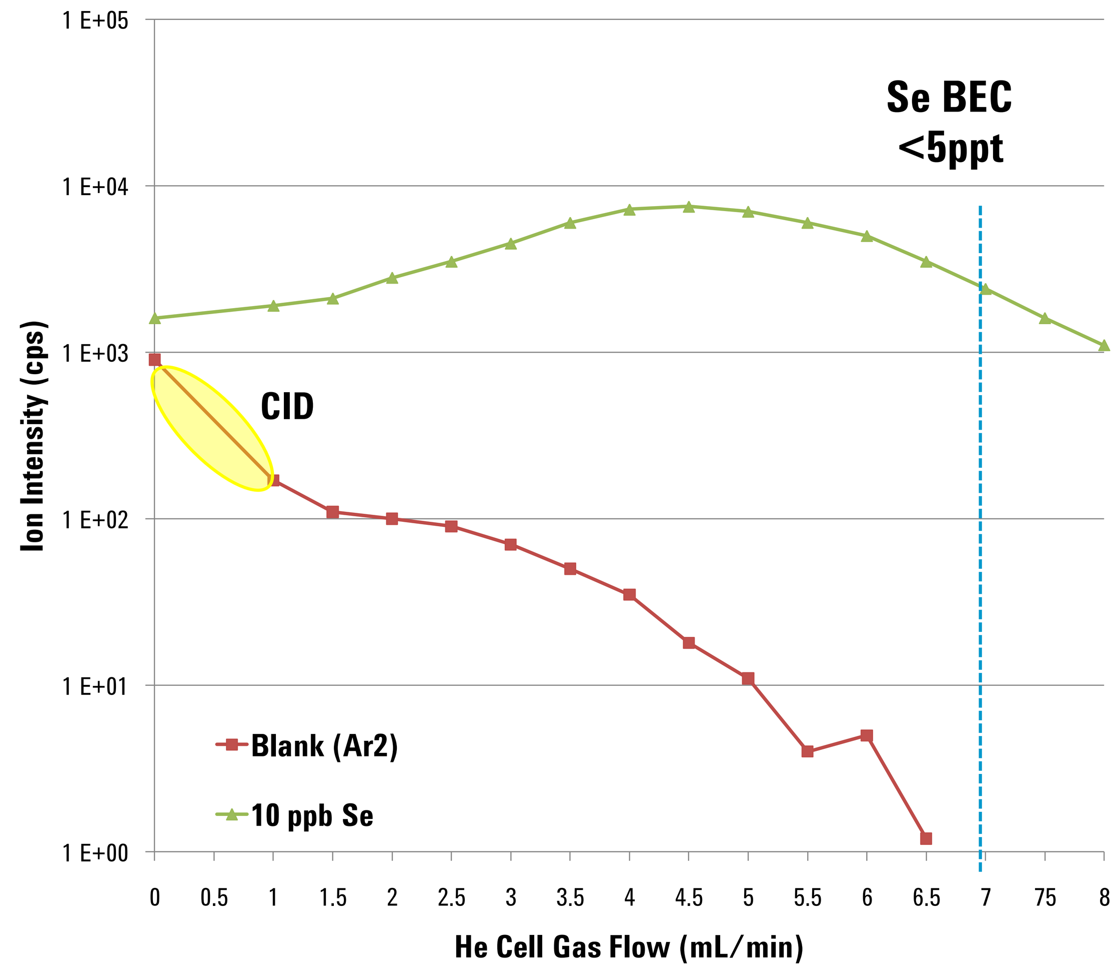
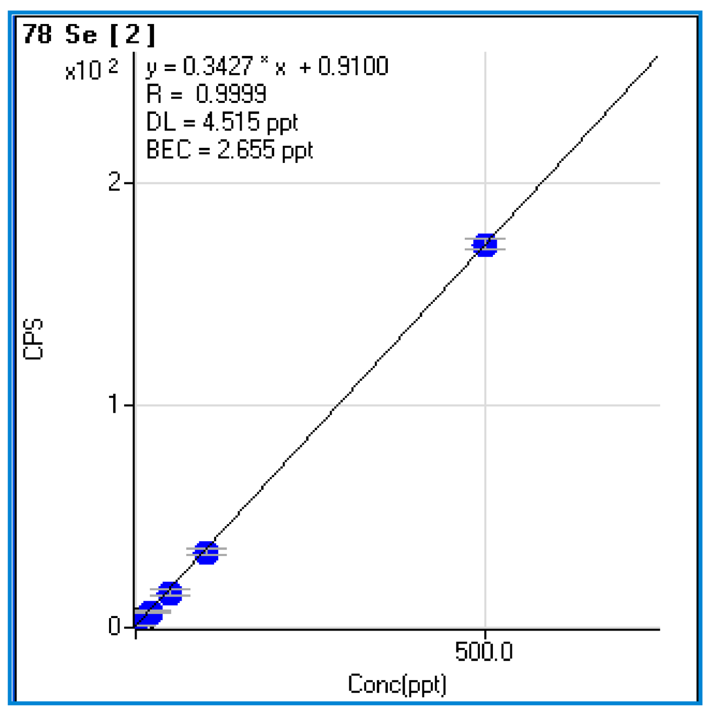


Figure 4. Cell gas optimization for Se/Ar_2 in ORS[3] He mode

The combination of improved separation of Se and Ar_2 ions due to the higher cell gas flow and higher collision energy, together with the effect of CID of the Ar_2 ions leads to an overall improvement in BEC and detection limit (DL) to less than 5ppt for ^{78}Se using He mode in the ORS[3], as shown in the calibration in Figure 5.



The improvement in DL for Se means that most applications can be addressed using only He mode. He mode offers more reliable removal of unknown interferences in complex and variable samples, and means that a single gas mode may be used for all elements. This is essential for transient signals and discrete sampling.

Figure 5. Calibration for ^{78}Se using ORS[3] in He mode. BEC 2.7ppt; DL 4.5ppt

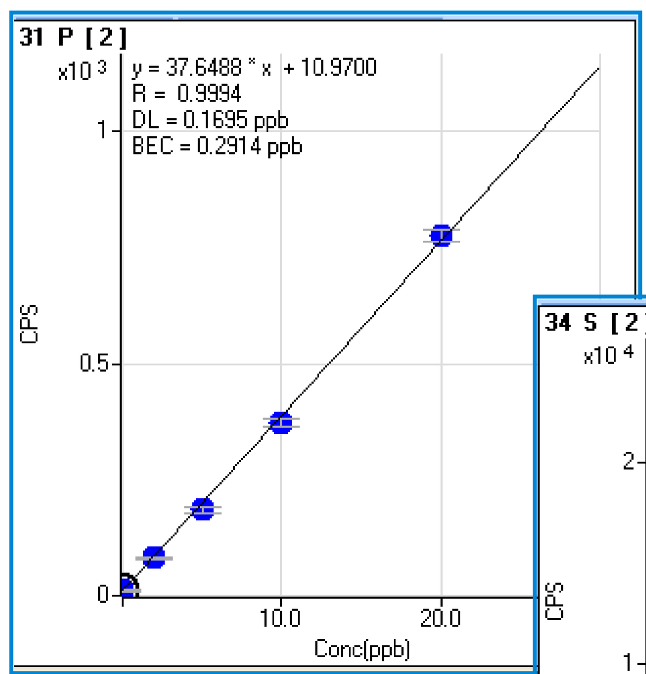


Figure 6. Calibration for ^{31}P using ORS[3] in He mode. BEC 291ppt, DL 170ppt

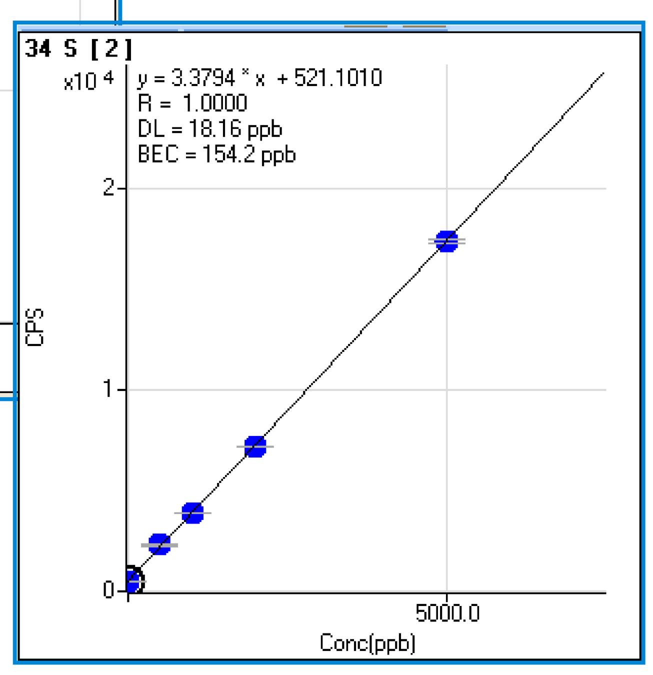


Figure 7. Calibration for ^{34}S using ORS[3] in He mode. BEC 154ppb, DL 18.2ppb

Figures 6 and 7 illustrate that the benefits of the high cell gas flow and high collision energy of ORS[3] also apply to other elements which suffer from intense background interferences, notably ^{31}P and ^{34}S (illustrated). ^{56}Fe measurement (not shown) is also improved for the same reason.

Conclusion

The practical benefits of He mode are well-established for multi-element analysis of variable sample matrices, and the introduction of the new ORS[3] collision/reaction cell now allows He mode to be applied to several elements that previously required reactive cell gases. Improved discrimination between analyte and polyatomic ions due to higher cell gas flow and collision energy, coupled with the promotion of collision induced dissociation, means that single ppt detection limits are now achievable for ^{78}Se, allowing this element to be measured in He mode along with the majority of other typical analytes.