Comparing Collision/Reaction Cell Modes for the Measurement of Interfered Analytes in Complex Matrices using the Agilent 7700 Series ICP-MS

Technical Overview

Abstract

Inductively coupled plasma mass spectrometry (ICP-MS) is a key analytical tool in many laboratories. It is used for elemental determinations across a wide range of analyses, including environmental, semiconductor, food safety, geological, chemical, petrochemical, nuclear, clinical, forensic, and research applications. Since the early publications during the development of ICP-MS, it has been apparent that one of the key limitations of the technique was the presence of molecular ions that overlap the preferred isotopes of several analytes. These molecular ions are typically called "polyatomic" ions, and are derived from combinations of the elements present in the plasma, the solvent and the sample matrix.

Strategies for reducing, removing or correcting for these polyatomic interferences vary, but most of the emphasis over the past 10 years has been on using collision/reaction cell (CRC) technology to selectively reduce the transmission of the interfering ions, thereby reducing the contribution of the interference at the analyte mass. Many publications have presented methods where a specific reaction gas is used to separate single, known interferences from single analyte isotopes. While this is of undoubted academic interest, the removal of a single, known interference from a single analyte is not relevant for the majority of real applications, where ICP-MS is used to determine multiple analytes in a range of complex and unknown sample matrices. This study compared no gas, reaction and collision modes for the measurement of multiple interfered analytes in the complex and variable matrices that are typically analyzed in many laboratories. The data demonstrate the superior performance achieved with helium (He) collision mode in the 3rd generation Octopole Reaction System (ORS^3) of the Agilent 7700 Series.

Agilent Technologies

Introduction

The Agilent 7700 Series ORS^3 is the culmination of development work that started with the original ORS, introduced on the Agilent 7500c ICP-MS in 2001. Conceived as a reaction cell, using H_2 cell gas to selectively remove intense interferences on interfered elements such as ^{40}Ca (overlapped by Ar), ^{56}Fe (overlapped by ArO) and ^{80}Se (overlapped by Ar_2), the ORS was also designed to operate in collision mode, using He cell gas. It quickly became apparent that He mode combined with interference removal by kinetic energy discrimination (KED) offered several key benefits, especially for the analysis of complex and variable samples. However, the ORS of the 7500c could not match the sensitivity specification of non-cell instruments, due to the use of an off-axis cell configuration, designed to protect the cell from matrix contamination. Subsequent developments led to the second generation ORS, used in the Agilent 7500ce, launched in 2004. With this development, the focus was on increasing ion transmission, while also improving robustness for high matrix sample analysis. This was achieved by moving the cell to an on-axis configuration, and placing an off-axis ion lens in front of it. The off-axis lens removes contaminants (such as neutrals and photons) prior to the cell, improving matrix tolerance and long-term stability.

The ORS^3 has been developed to maximize the capability of He mode, allowing this simple and consistent mode to be applied to a wider range of analytes and sample types than ever before. In most common applications (with the exception of semiconductor), the use of reactive cell gases is no longer required, with all the benefits for method development and routine operation that this provides.

Much of the published work relating to collision/reaction cell (CRC) technology has focused on removing well-characterized interferences by adding a specific reaction gas to the cell. This approach has three important limitations, which are rarely addressed in the published work:

1) Each reaction gas will only remove interferences which react with that gas. If several matrix-based polyatomic interferences occur at the same analyte mass, not all the polyatomics will react with the selected cell gas, so some residual interferences remain. In the same way, reaction gases are rarely suitable for multi-element analysis, because different analytes suffer overlap from different interferences, not all of which will react with the chosen cell gas.

2) All reaction gases will react with matrix, interference and analyte ions, to create new cell-formed reaction product ions; these may appear as new interferences on other analytes, and the new interferences will vary depending on the sample matrix.

3) Any reactive cell gas will react with some of the analyte ions, as well as the target polyatomic(s). This causes signal loss for the analyte(s), degrading detection limits.

The comparative tests discussed here investigate the practical effect of these potential issues, and assess which mode, collision or reaction, is more effective for multi-element analysis in a complex sample matrix. The matrices in which the tests were carried out are detailed in Table 1.

Table 1. Individual Matrices and Combined Mixed Matrix Composition

Matrix component	Solution used
N	5 % HNO_3
Cl	5 % HCl
S	1 % H_2SO_4
C	1 % methanol
Na	200 ppm Na
Ca	200 ppm Ca
P	500 ppm P
Mix	All of the above

The mixed matrix was developed as a result of a contract laboratory ICP-MS evaluation, in which samples of many different matrices were provided for analysis. The matrices covered a range of typical environmental sample types, including soil extracts, waste waters, trade effluents, leachates and "one-off" samples, such as rainwater runoff and delivery tanker washout samples. All of the matrix components in the mixed matrix sample were present at comparable levels in one or more of the sample types evaluated by this laboratory, and all may be present at variable and unknown levels in many common sample types. Therefore, this analysis provides a tough but very realistic test for any ICP-MS instrument.

Further matrix components may be added (such as Si, K, Al, etc), but each additional matrix component increases the possibility of adding trace levels of the analytes of interest, as contaminants in the matrix.

Analytes

Since ICP-MS is most typically used for multi-element analysis, our investigation focused on all of the elements in the mass range from 45 to 80, which represents the most interfered region of the ICP-MS spectrum in most sample types. This mass range covers all the preferred isotopes of all the analytes from Sc (mass 45) to Se (mass 78). A full list of the elements measured and the isotopes used is given in Table 2.

Matrix Components

Table 2 also lists the potential polyatomic interferences which might arise in the complex mixed matrix described in Table 1. It should be noted that at least one polyatomic interference can occur on every isotope of every element in this mass range, and also that the various polyatomics which overlap each analyte mass typically arise from different matrix components. This is the main reason why single-element and single-matrix tests of CRC performance are largely irrelevant.

Isotope	Principal Interfering Species (mixed matrix)
^{45}Sc	$^{13}C^{16}O_2$, $^{12}C^{16}O_2H$, ^{44}CaH, $^{32}S^{12}CH$, $^{32}S^{13}C$, $^{33}S^{12}C$
^{47}Ti	$^{31}P^{16}O$, ^{46}CaH, $^{35}Cl^{12}C$, $^{32}S^{14}NH$, $^{33}S^{14}N$
^{49}Ti	$^{31}P^{18}O$, ^{48}CaH, $^{35}Cl^{14}N$, $^{37}Cl^{12}C$, $^{32}S^{16}OH$, $^{33}S^{16}O$
^{50}Ti	$^{34}S^{16}O$, $^{32}S^{18}O$, $^{35}Cl^{14}NH$, $^{37}Cl^{12}CH$
^{51}V	$^{35}Cl^{16}O$, $^{37}Cl^{14}N$, $^{34}S^{16}OH$
^{52}Cr	$^{36}Ar^{16}O$, $^{40}Ar^{12}C$, $^{35}Cl^{16}OH$, $^{37}Cl^{14}NH$, $^{34}S^{18}O$
^{53}Cr	$^{36}Ar^{16}OH$, $^{40}Ar^{13}C$, $^{37}Cl^{16}O$, $^{35}Cl^{18}O$, $^{40}Ar^{12}CH$
^{54}Fe	$^{40}Ar^{14}N$, $^{40}Ca^{14}N$, $^{23}Na^{31}P$
^{55}Mn	$^{37}Cl^{18}O$, $^{23}Na^{32}S$, $^{23}Na^{31}PH$
^{56}Fe	$^{40}Ar^{16}O$, $^{40}Ca^{16}O$
^{57}Fe	$^{40}Ar^{16}OH$, $^{40}Ca^{16}OH$
^{58}Ni	$^{40}Ar^{18}O$, $^{40}Ca^{18}O$, $^{23}Na^{35}Cl$
^{59}Co	$^{40}Ar^{18}OH$, $^{43}Ca^{16}O$, $^{23}Na^{35}ClH$
^{60}Ni	$^{44}Ca^{16}O$, $^{23}Na^{37}Cl$
^{61}Ni	$^{44}Ca^{16}OH$, $^{38}Ar^{23}Na$, $^{23}Na^{37}ClH$
^{63}Cu	$^{40}Ar^{23}Na$, $^{12}C^{16}O^{35}Cl$, $^{12}C^{14}N^{37}Cl$, $^{31}P^{32}S$, $^{31}P^{16}O_2$
^{64}Zn	$^{32}S^{16}O_2$, $^{32}S_2$, $^{36}Ar^{12}C^{16}O$, $^{38}Ar^{12}C^{14}N$, $^{48}Ca^{16}O$
^{65}Cu	$^{32}S^{16}O_2H$, $^{32}S_2H$, $^{14}N^{16}O^{35}Cl$, $^{48}Ca^{16}OH$
^{66}Zn	$^{34}S^{16}O_2$, $^{32}S^{34}S$, $^{33}S_2$, $^{48}Ca^{18}O$
^{67}Zn	$^{32}S^{34}SH$, $^{33}S_2H$, $^{48}Ca^{18}OH$, $^{14}N^{16}O^{37}Cl$, $^{16}O_2{}^{35}Cl$
^{68}Zn	$^{32}S^{18}O_2$, $^{34}S_2$
^{69}Ga	$^{32}S^{18}O_2H$, $^{34}S_2H$, $^{16}O_2{}^{37}Cl$
^{70}Zn	$^{34}S^{18}O_2$, $^{35}Cl_2$
^{71}Ga	$^{34}S^{18}O_2H$, $^{35}Cl_2H$, $^{40}Ar^{31}P$
^{72}Ge	$^{40}Ar^{32}S$, $^{35}Cl^{37}Cl$, $^{40}Ar^{16}O_2$
^{73}Ge	$^{40}Ar^{32}SH$, $^{40}Ar^{33}S$, $^{35}Cl^{37}ClH$, $^{40}Ar^{16}O_2H$
^{74}Ge	$^{40}Ar^{34}S$, $^{37}Cl_2$
^{75}As	$^{40}Ar^{34}SH$, $^{40}Ar^{35}Cl$, $^{40}Ca^{35}Cl$, $^{37}Cl_2H$
^{77}Se	$^{40}Ar^{37}Cl$, $^{40}Ca^{37}Cl$
^{78}Se	$^{40}Ar^{38}Ar$
^{80}Se	$^{40}Ar_2$, $^{40}Ca_2$, $^{40}Ar^{40}Ca$, $^{32}S_2{}^{16}O$, $^{32}S^{16}O_3$

Table 1. Analytes measured in matrix tests, together with possible polyatomic overlaps derived from the mixed matrix solution. Highlighted isotopes are preferred analytical masses.

Instrumentation: Tuning and Data Acquisition

The Agilent 7700x was used to measure each sample in each of the 3 modes (no gas, helium and hydrogen), using standard Agilent-recommended autotuning for robust tuning conditions (around 1.0 % CeO/Ce). In addition to the use of consistent sample introduction parameters and plasma conditions, consistent ion lens, cell gas flow rate and cell voltage settings were used for the measurement of all of the analytes and matrices within each cell mode. Standard cell gas flow rates and KED bias voltages were used in each mode.

A method was defined with all three cell gas modes run in the following order: no gas, H_2, He. The sample sequence was prepared, with a two-point multi-element external calibration at 0 ppb and 10 ppb, stabilized with 0.1 % HNO_3 (the zero matrix calibration reference). All the remaining blank (unspiked) matrices were then measured against this external calibration. No internal standards were used. Each sample was measured only once, with the system switching between cell modes during the acquisition for each sample. The standard Agilent multistep rinse program was used, in conjunction with pre-emptive rinse.

Results and Discussion

The concentration of each analyte in each matrix was calibrated against the standards in 0.1 % HNO_3, and the measured concentrations in each cell gas mode were plotted against the matrix name. This gave a series of comparison plots, showing the background equivalent concentration (BEC) for each analyte in each gas mode, plotted against the matrix. Since all the samples in these plots were unspiked matrices, all the results should have been zero, so any positive result indicates the presence of a polyatomic interference or trace contamination of that analyte in the matrix. Example plots are shown, illustrating the typical performance observed.

Removal of Matrix-Based Interferences

Figure 1 shows the BEC for As (measured at mass 75) in each gas mode, plotted against each matrix. As might be expected, the no gas mode data showed a high apparent concentration of As in the 5 % HCl matrix, due to the interference from ArCl which contributes to the signal at mass 75. The apparent As concentration in no gas mode was much higher in the mixed matrix (the final point on the x-axis), than in the HCl alone (about 27 ppb, compared to about 11 ppb). This is because

the mix contained the Ca from the 200 ppm Ca solution, as well as the Cl from the 5 % HCl. This new combination led to the formation of a new CaCl polyatomic interference on As, which was not present in any of the single-component solutions.

By contrast, the results for As in He mode were consistently at a low level in all the single matrices and the mix, indicating effective removal of both the ArCl and the CaCl interferences in these unspiked matrices.

Figure 1 shows that the ArCl interference was also removed effectively in reaction mode (H_2 cell gas), since ArCl is highly reactive with H_2. However, while H_2 mode removed the ArCl interference on As, it did not completely remove the CaCl, illustrating the point that not all of the interferences at any given analyte mass may react with the same reaction gas.

This comparison highlights a common problem of reactive cell gases, where a method may be developed using one specific sample type, but then the chosen reaction gas fails to remove interferences successfully in routine use, where the unknown sample matrices do not match the original sample type.

As shown in Figure 2, a similar comparison can be observed for ^{47}Ti (which suffers from polyatomic interferences from PO and CCl), and ^{59}Co (CaO/CaOH), ^{60}Ni (CaO/CaOH) and ^{63}Cu (ArNa) also suffered from residual interferences in H_2 mode. All of these interferences were effectively removed in He mode.

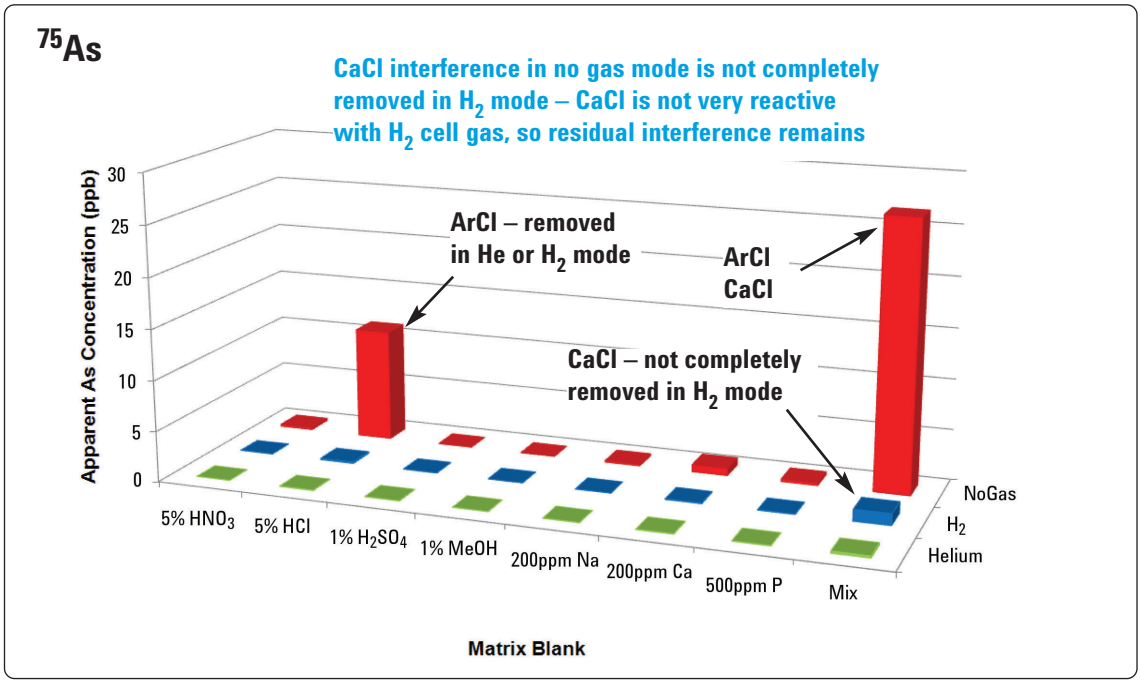

Figure 1. Comparison plot of ^{75}As BEC vs sample matrix for three cell modes.

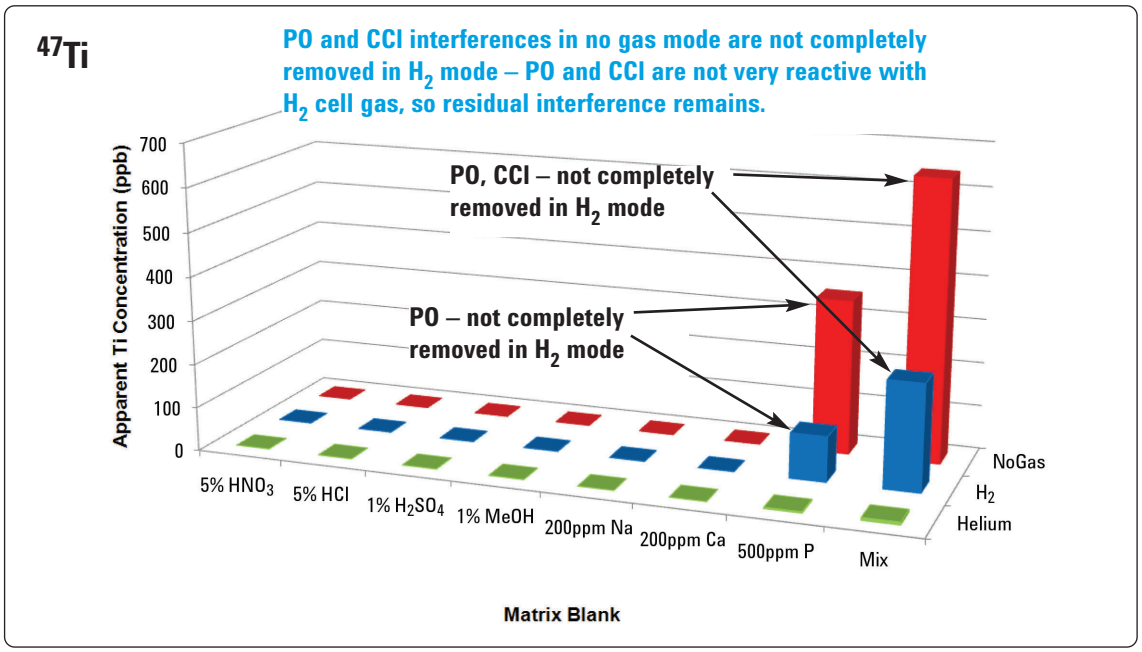

Figure 2. Comparison plot of ^{47}Ti BEC vs sample matrix for three cell modes.

Creation of New Cell-Formed Interferences

For some combinations of analyte and matrix, another important problem of reactive cell gases was observed, as illustrated in Figure 3 for ^{45}Sc in the Ca matrix.

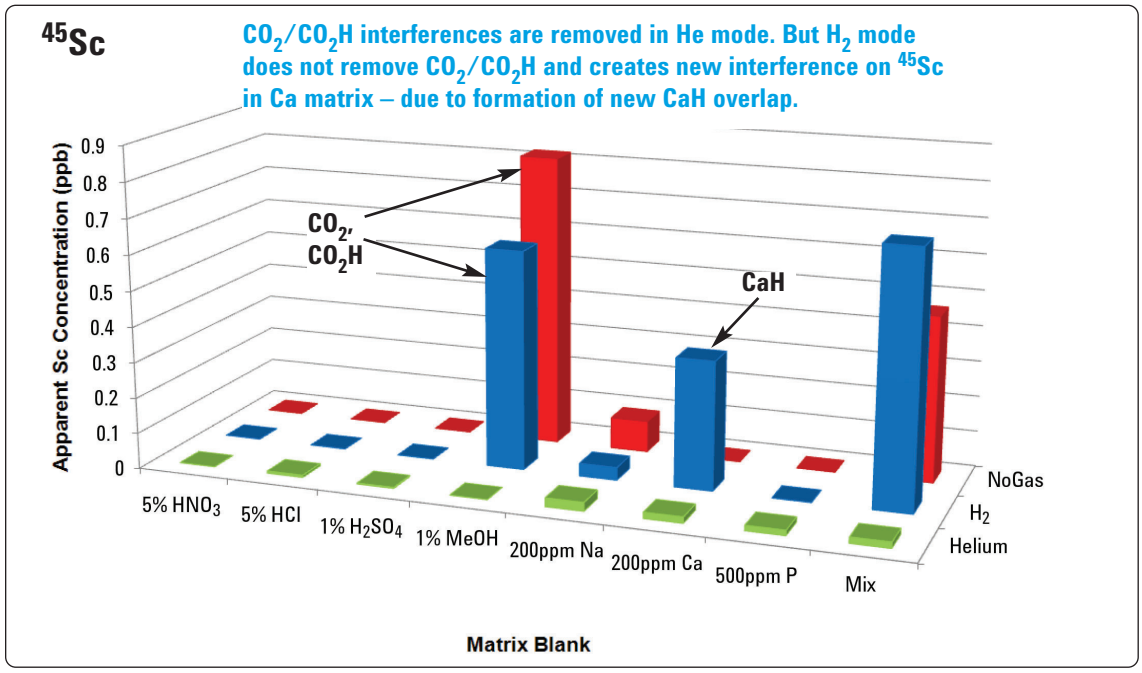

Figure 3. Comparison plot of ^{45}Sc BEC vs sample matrix for three cell modes.

In no gas mode, a polyatomic interference was observed on Sc in the 1 % acetic acid matrix, due to the formation of CO_2 and CO_2H interferences. These interferences were reduced but not completely removed in H_2 mode. It is possible that the CO_2 was reduced, but through a reaction process that led to an increase in CO_2H.

However, in the Ca matrix, the level of polyatomic interference on Sc was very low in no gas mode and He mode, but much higher when H_2 cell gas was used. This is because H_2 reacts with Ca to form a new cell-formed reaction product ion, ^{44}CaH, greatly increasing the interference on ^{45}Sc. By contrast, the apparent Sc concentration measured in He mode was low and consistent in all the single matrix blanks and in the mix, again illustrating effective removal of all the polyatomic interferences in He mode. He is inert, so no new polyatomic ions are formed in the cell, regardless of the sample composition.

As shown in Figure 4, a similar pattern was observed for ^{65}Cu (S_2H and SO_2H), and ^{51}V and ^{52}Cr were also affected by the creation of new cell-formed polyatomic ions (SOH on ^{51}V, and ClOH on ^{52}Cr), which led to an increased level of interference in H_2 mode compared to no gas mode. All of these interferences were removed effectively in He mode.

Loss of Analyte Sensitivity Due to Reaction with Cell Gas

The third potential issue with reaction mode is the loss of analyte sensitivity as a result of the analyte ions reacting with the cell gas. This effect is partly responsible for the very poor performance seen for Cu in H_2 mode, and is illustrated more clearly in Figure 5. Figure 5a shows that in no gas mode, without any added matrix, the spectrum of transition elements reflected the relative intensities expected from the natural isotopic abundance and degree of ionization of each element.

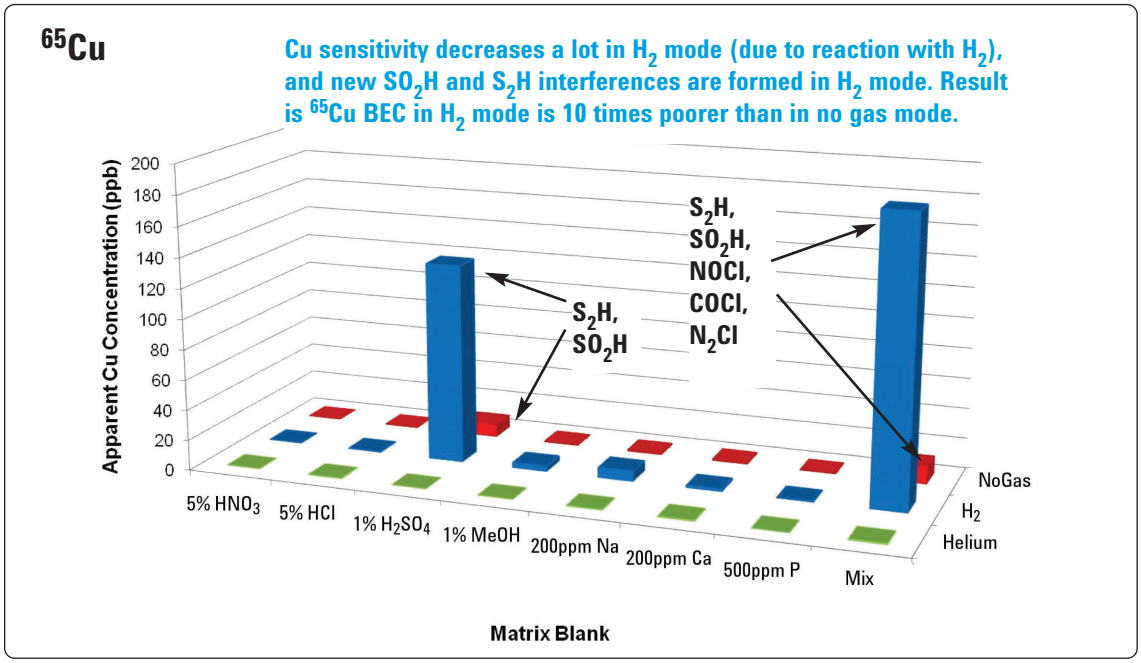

Figure 4. Comparison plot of ^{65}Cu BEC vs sample matrix for three cell modes.

In He mode (Figure 5b), this general pattern of peak intensities was maintained, although with a slight increase in mass bias (lower transmission for lighter elements), due to scattering of the lighter ions. In He mode, the intense peaks from ArO and Ar_2 interferences (the highest peaks in the no gas spectrum) were also removed, so the ^{56}Fe and $^{78}Se/^{80}Se$ isotopes also matched the expected abundances.

After correction for mass bias, isotopic abundance and degree of ionization, all the peaks in the He mode spectrum would lie on a consistent "mass/response" curve. This allows reliable calibration in semiquantitative analysis, where uncalibrated elements are quantified by reference to their response relative to a few calibrated elements across the mass range.

In H_2 mode (Figure 5c), by contrast, the peak pattern was completely different from the reference spectrum in no gas mode. The relative intensities of the Ni and Cu peaks in particular were dramatically lower, but also the V, Cr, Co, As and, to a lesser extent, Fe, were all reduced compared to the

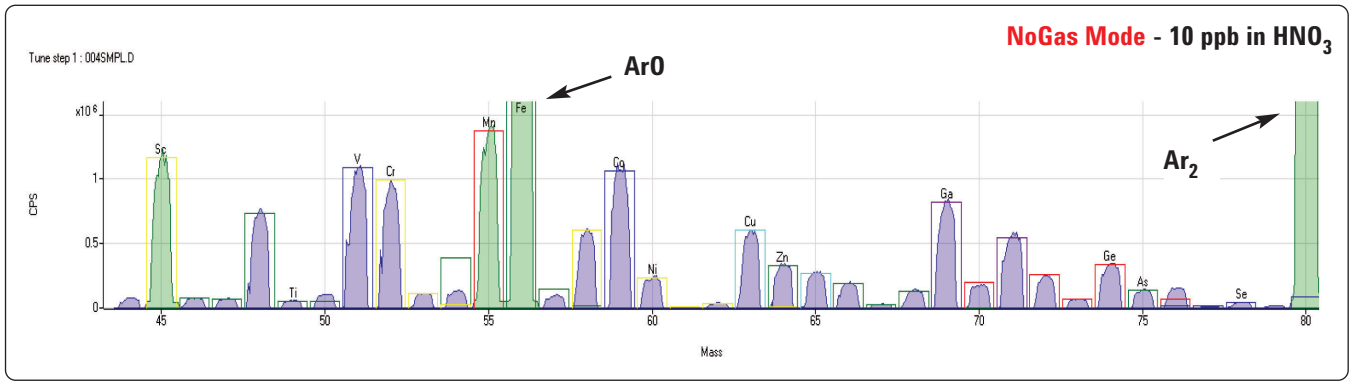

Figure 5a. Relative sensitivity for analytes from Sc to Se in no gas mode.

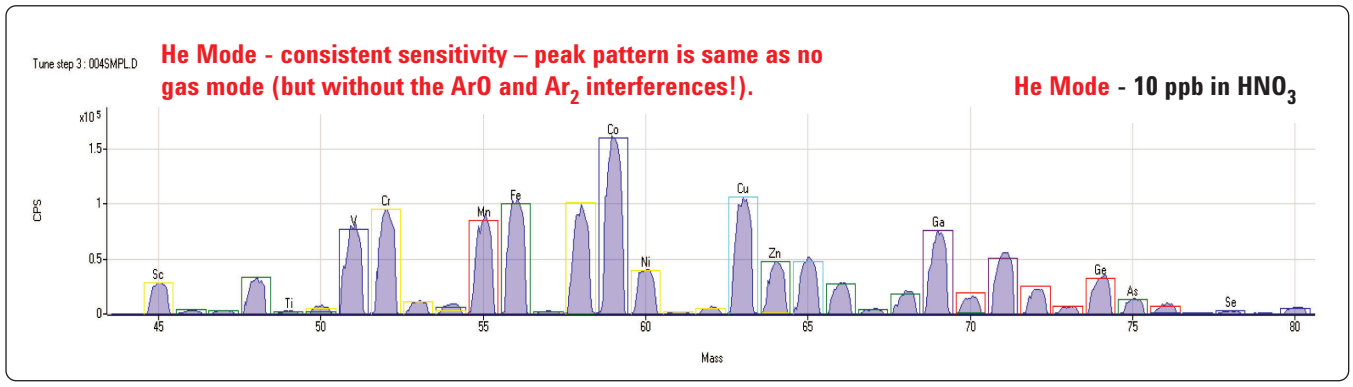

Figure 5b. Relative sensitivity for analytes from Sc to Se in He mode.

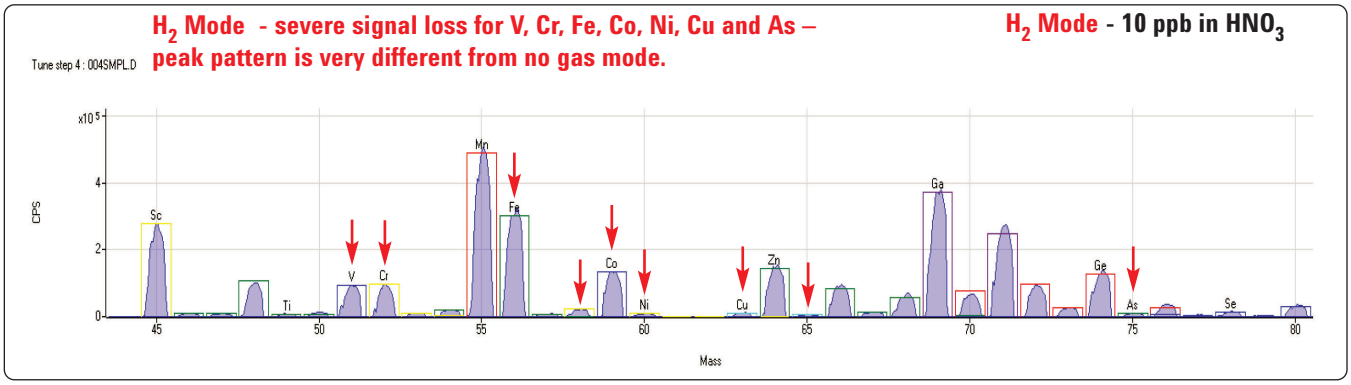

Figure 5c. Relative sensitivity for analytes from Sc to Se in H_2 (reaction) mode.

pattern observed in no gas mode. It is clear that no reliable mass/response curve could be fitted to this data, as the loss of sensitivity was so different between adjacent analytes.

This comparison highlights other key benefits of He mode, which are that it simplifies method setup and improves the quality of data obtained by semiquantitative calibration. H_2 mode does not maintain a consistent relationship between different analytes and cannot therefore be used successfully for semiquant or "non-specific" calibration. In terms of the actual sensitivity loss, the signal reduction for Cu in H_2 mode is of the order of 95 to 99 %. This dramatic and variable loss of analyte sensitivity by reaction is another reason why reactive cell gases are not commonly used for multi-element applications.

Conclusions

In the investigations discussed, it has been shown that several serious problems can occur when H_2 cell gas is used during the measurement of the first row transition elements in a complex matrix. These problems are:

1) Failure to remove unreactive polyatomic ions, leading to residual interferences
2) Creation of new, cell-formed reaction product ions
3) Loss of sensitivity for several analytes, due to reaction with the cell gas.

The net result of these three problems is that He mode is not only simpler and more consistent in operation, but also generates more reliable data than H_2 mode for multi-element analysis of complex samples under a single set of operating conditions.

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