Unmatched Removal of Spectral Interferences in ICP-MS Using the Agilent Octopole Reaction System with Helium Collision Mode

Application

Metals Analysis

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Abstract

Many routine laboratories have adopted ICP-MS as their primary technique for metals analysis due to its simple operation as a multi-element analyzer. However, despite its higher performance for the targeted removal of specific interferences, collision/reaction cell (CRC) ICP-MS remains relatively understudied in terms of its multi-element capability. This work demonstrates that the Agilent 7500ce ICP-MS can be operated with a single set of He cell gas conditions, to provide effective interference removal for a range of elements in a challenging and complex sample matrix.

Introduction

ICP-MS is an immensely powerful multi-element analytical technique, but it does suffer from some well-documented spectral interferences, which can be especially problematic when complex and variable samples are analyzed. Most interferences in ICP-MS arise due to an overlap from a molecular (or polyatomic) ion at the same nominal mass as the analyte of interest. Commonly reported interferences can be broadly divided into two groups: those derived from the plasma and aqueous solution (plasma-based), such as $^{40}\mathrm{Ar}$, $^{40}\mathrm{Ar}^{16}\mathrm{O}$, and $^{40}\mathrm{Ar}^{38}\mathrm{Ar}$, and those derived from sample matrix components (matrix-based), such as $^{35}\mathrm{Cl}^{16}\mathrm{O}$, and $^{32}\mathrm{S}^{34}\mathrm{S}$. Plasma-based polyatomic ions are both predictable and reasonably constant, regardless of sample matrix, whereas matrix-based polyatomic ions are less predictable and vary with sample matrix components and their relative concentrations.

Recent advances in CRC technology have led to dramatic improvements in the analysis of interfered elements which previously proved difficult or impossible to measure at required levels in certain sample matrices. In a CRC ICP-MS, the cell is typically pressurized with a reactive gas that reacts with the interference (referred to as reaction mode). Attenuation of the interfering species occurs by one of several different processes depending on the gas and the interference. However, in practice, “reaction mode-only” CRCs limit the system to the removal of single interfering ions from single analytes [1–8], using highly reactive gases and specific measurement conditions. Some instruments use “simpler” or less reactive cell gas such as H_2, but its use is limited mainly to plasma-based interferences, as it reacts slowly or not at all with matrix-based interferences which are much more difficult to remove.

Helium (He) Collision Mode

The development of the Agilent Octopole Reaction System (ORS) introduced a new and much more powerful mode of CRC operation – He collision mode – which uses an inert collision gas to remove all polyatomic species based on their size rather

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than their relative reactivity with a reaction gas. Since all polyatomics are larger than analyte ions of the same mass, their larger cross-section means that they suffer more collisions with the cell gas and so lose more energy as they progress through the pressurized region. On arrival at the cell exit, the large cross section polyatomic species all have distinctly lower ion energy (due to collisions with the He cell gas) than the analyte ions and so can be prevented from leaving the cell using a stopping voltage, allowing only the analytes to pass through to the analyzer. This separation process is known as kinetic energy discrimination (KED), and this simple yet extremely effective approach offers a number of significant analytical advantages over reaction mode.

Advantages of He Collision Mode:

- In contrast with a reactive cell gas, He is inert - so does not react with the sample matrix - no new interferences are formed in the cell
- As He is inert, it does not react with and cause signal loss for analyte or internal standard ions
- ALL interferences (plasma-based AND matrix-based) are removed or attenuated so multi-element screening or semiquant analysis can be combined with effective interference removal
- Since He collision mode is not interference-specific, multiple interferences can be removed from the same analyte (or different analytes) simultaneously [9, 10]
- No prior knowledge of the sample matrix is required, and no method development is required, in contrast to the extensive, analyte- and matrix-specific method development which is required for any reactive mode of interference removal [11]
- He collision mode can be applied to every sample, every matrix, and the same setup (gas flow rate) is used for every application
- No cell voltages to set up or optimize
- NO interference correction equations are used

Why Can't Other CRC-ICP-MS Use He Collision Mode?

To work properly, He collision mode requires efficient analyte/interference separation by KED, which requires two conditions to be met: first, the energy of all the ions entering the cell must be very tightly controlled. Agilent's unique ShieldTorch interface insures a very narrow ion energy spread of 1 eV: its physically grounded shield plate provides better control of initial ion energy than electrically grounded plasma designs (such as balanced, center-tapped or interlaced coils). Second, in the cell, polyatomic species must experience a sufficiently high number of collisions to differentiate them from the analyte ions at the cell exit. In the Agilent ORS this is achieved by the use of an octopole ion guide – the only implementation of an octopole cell in ICP-MS. There are two key benefits to the use of an octopole cell:

- Octopoles have a small internal diameter. As a result, the cell entrance and exit apertures are small – so the cell operates at relatively higher pressure compared to quadrupole or hexapole cells which increases ion/gas collisions.
- Octopoles also have better focusing efficiency than hexapole and quadrupole ion guides. The ion beam is tightly focused, which insures good ion transmission and high sensitivity at its higher cell operating pressure.

Only the Agilent ORS combines the ShieldTorch interface with an octopole cell and so only the Agilent ORS can effectively use He collision mode.

Testing He Collision Mode – a Worst Case Scenario

A synthetic sample matrix was prepared to give rise to multiple interferences across a range of common analytes and test the ability of He collision mode to remove all overlapping polyatomic species. A standard solution was prepared, containing 1% HNO_3, 1% HCl and 1% H_2SO_4 (all UpA UltraPure Reagents, Romil, Cambridge, UK), 1% Butan-1-ol (SpS Super Purity, Romil, Cambridge, UK) and 100 mg/L (ppm) each of Na and Ca (both prepared from 10,000 mg/L Spex CertiPrep Assurance single element standards), to simulate a very complex natural sample matrix. Table 1 summarizes the potential polyatomic species in this sample matrix, illustrating that practically every element in the mid-mass region (from 50 to 80 amu) suffers from multiple interferences. This makes the accurate determination of these elements in complex sample matrices extremely challenging for conventional ICP-MS, as the complex nature of the multiple interferences means mathematical corrections will be unreliable. This also illustrates why reactive cell gases are unsuitable for the multi-element analysis of complex samples; no single reaction gas can be effective for a range of polyatomic ions, each of which will have different reactivity with any given reactive cell gas. However, every interference shown in Table 1 is a polyatomic ion and can therefore be attenuated effectively using a single set of He collision mode conditions. Two sets of spectra were acquired to show the ability of the He collision mode to remove multiple interferences; one in no-gas mode and the second with He added to the cell. No data correction or background subtraction was applied. Finally, a 5-ppb multi-element spike was added to the matrix and spectra acquired to confirm the recovery of all analytes and check for correct isotopic fit.

Table 1. Principal Polyatomic Interferences from an Aqueous Matrix Containing N, S, Cl, C, Na, and Ca

Isotope	Principal interfering species
$\mathrm{^{51}V}$	$\mathrm{^{35}Cl^{16}O}$, $\mathrm{^{37}Cl^{14}N}$
$\mathrm{^{52}Cr}$	$\mathrm{^{36}Ar^{16}O}$, $\mathrm{^{40}Ar^{12}C}$, $\mathrm{^{35}Cl^{16}OH}$, $\mathrm{^{37}Cl^{14}NH}$
$\mathrm{^{53}Cr}$	$\mathrm{^{36}Ar^{16}OH}$, $\mathrm{^{40}Ar^{13}C}$, $\mathrm{^{37}Cl^{16}O}$, $\mathrm{^{35}Cl^{18}O}$, $\mathrm{^{40}Ar^{12}CH}$
$\mathrm{^{54}Fe}$	$\mathrm{^{40}Ar^{14}N}$, $\mathrm{^{40}Ca^{14}N}$
$\mathrm{^{55}Mn}$	$\mathrm{^{37}Cl^{18}O}$, $\mathrm{^{23}Na^{32}S}$
$\mathrm{^{56}Fe}$	$\mathrm{^{40}Ar^{16}O}$, $\mathrm{^{40}Ca^{16}O}$
$\mathrm{^{57}Fe}$	$\mathrm{^{40}Ar^{16}OH}$, $\mathrm{^{40}Ca^{16}OH}$
$\mathrm{^{58}Ni}$	$\mathrm{^{40}Ar^{18}O}$, $\mathrm{^{40}Ca^{18}O}$, $\mathrm{^{23}Na^{35}Cl}$
$\mathrm{^{59}Co}$	$\mathrm{^{40}Ar^{18}OH}$, $\mathrm{^{43}Ca^{16}O}$
$\mathrm{^{60}Ni}$	$\mathrm{^{44}Ca^{16}O}$, $\mathrm{^{23}Na^{37}Cl}$
$\mathrm{^{61}Ni}$	$\mathrm{^{44}Ca^{16}OH}$, $\mathrm{^{38}Ar^{23}Na}$, $\mathrm{^{23}Na^{37}ClH}$
$\mathrm{^{63}Cu}$	$\mathrm{^{40}Ar^{23}Na}$, $\mathrm{^{12}C^{16}O^{35}Cl}$, $\mathrm{^{12}C^{14}N^{37}Cl}$
$\mathrm{^{64}Zn}$	$\mathrm{^{32}S^{16}O_2}$, $\mathrm{^{32}S_2}$, $\mathrm{^{36}Ar^{12}C^{16}O}$, $\mathrm{^{38}Ar^{12}C^{14}N}$, $\mathrm{^{48}Ca^{16}O}$
$\mathrm{^{65}Cu}$	$\mathrm{^{32}S^{16}O_2H}$, $\mathrm{^{32}S_2H}$, $\mathrm{^{14}N^{16}O^{35}Cl}$, $\mathrm{^{48}Ca^{16}OH}$
$\mathrm{^{66}Zn}$	$\mathrm{^{34}S^{16}O_2}$, $\mathrm{^{32}S^{34}S}$, $\mathrm{^{33}S_2}$, $\mathrm{^{48}Ca^{18}O}$
$\mathrm{^{67}Zn}$	$\mathrm{^{32}S^{34}SH}$, $\mathrm{^{33}S_2H}$, $\mathrm{^{48}Ca^{18}OH}$, $\mathrm{^{14}N^{16}O^{37}Cl}$, $\mathrm{^{16}O_2{}^{35}Cl}$
$\mathrm{^{68}Zn}$	$\mathrm{^{32}S^{18}O_2}$, $\mathrm{^{34}S_2}$
$\mathrm{^{69}Ga}$	$\mathrm{^{32}S^{18}O_2H}$, $\mathrm{^{34}S_2H}$, $\mathrm{^{16}O_2{}^{37}Cl}$
$\mathrm{^{70}Zn}$	$\mathrm{^{34}S^{18}O_2}$, $\mathrm{^{35}Cl_2}$
$\mathrm{^{71}Ga}$	$\mathrm{^{34}S^{18}O_2H}$
$\mathrm{^{72}Ge}$	$\mathrm{^{40}Ar^{32}S}$, $\mathrm{^{35}Cl^{37}Cl}$, $\mathrm{^{40}Ar^{16}O_2}$
$\mathrm{^{73}Ge}$	$\mathrm{^{40}Ar^{33}S}$, $\mathrm{^{35}Cl^{37}ClH}$, $\mathrm{^{40}Ar^{16}O_2H}$
$\mathrm{^{74}Ge}$	$\mathrm{^{40}Ar^{34}S}$, $\mathrm{^{37}Cl_2}$
$\mathrm{^{75}As}$	$\mathrm{^{40}Ar^{34}SH}$, $\mathrm{^{40}Ar^{35}Cl}$,$\mathrm{^{40}Ca^{35}Cl}$
$\mathrm{^{77}Se}$	$\mathrm{^{40}Ar^{37}Cl}$, $\mathrm{^{40}Ca^{37}Cl}$
$\mathrm{^{78}Se}$	$\mathrm{^{40}Ar^{38}Ar}$
$\mathrm{^{80}Se}$	$\mathrm{^{40}Ar_2}$, $\mathrm{^{40}Ca_2}$, $\mathrm{^{40}Ar^{40}Ca}$

Instrumentation

An Agilent 7500ce ICP-MS was optimized using the typical tuning conditions for high and variable sample matrices (plasma conditions optimized as usual for ~0.8% CeO/Ce). No attempt was made to optimize any parameter for the targeted removal of any specific interference. 5.5 mL/min He gas (only) was added to the cell for the collision mode measurements.

Comparison of Spectra

The background spectrum obtained in no-gas mode is shown in Figure 1a, together with the same spectrum (same mass range and intensity scale) under He collision mode conditions, in Figure 1b. From Figure 1a, it is clear that the normal background components of the argon plasma gas and aqueous sample solution (Ar, O, H), together with the additional components of the synthetic sample matrix ($\mathrm{HNO_3}$, HCl, $\mathrm{H_2SO_4}$, butanol, Ca and Na), lead to the formation of several high intensity background peaks in the no-gas mode spectrum, notably $\mathrm{^{40}Ar^{16}O^+}$ and $\mathrm{^{40}Ar_2{}^+}$ from the plasma, but also $\mathrm{^{40}Ar^{12}C^+}$, $\mathrm{^{32}S_2{}^+}$, $\mathrm{^{35}Cl^{16}O^+}$, etc, from the matrix. These high intensity background peaks show why several interfered elements ($\mathrm{^{56}Fe}$, $\mathrm{^{78}Se}$ and $\mathrm{^{80}Se}$, $\mathrm{^{52}Cr}$ in a carbon matrix, $\mathrm{^{64}Zn}$ in a sulfur matrix) have traditionally been considered as difficult elements for ICP-MS.

When helium is added to the cell (He collision mode conditions) all of these high intensity background peaks are removed from the spectrum, (Figure 1b – same sample, same intensity scale as Figure 1a) demonstrating the effectiveness and the universal applicability of He collision mode. Figures 2a and 2b are the same two spectra as in Figure 1, but with the vertical scale expanded 100x. Many more, lower intensity, matrix-derived polyatomic species are now observed. These interferences, though present at lower levels than the plasma-based polyatomic ions, have the potential to cause more serious errors in routine sample analysis, as their presence and intensity is dependent on matrix composition, which, in routine laboratories, may be variable and unknown. At this expanded scale, it is clear that the use of He collision mode has reduced the background species to very low levels, including the high intensity plasma-based species ArO^+ and Ar_2^+. The only peaks clearly visible in He collision mode (Figure 2b) on this scale are Fe and Zn (the peak template confirms the Zn isotopic pattern at *m/z* 64, 66, and 68), due to trace level contamination present in the matrix components. By contrast, in no-gas mode (Figure 2a), almost every isotope of every element in this mass region has an overlap from at least one matrix-derived polyatomic interference.

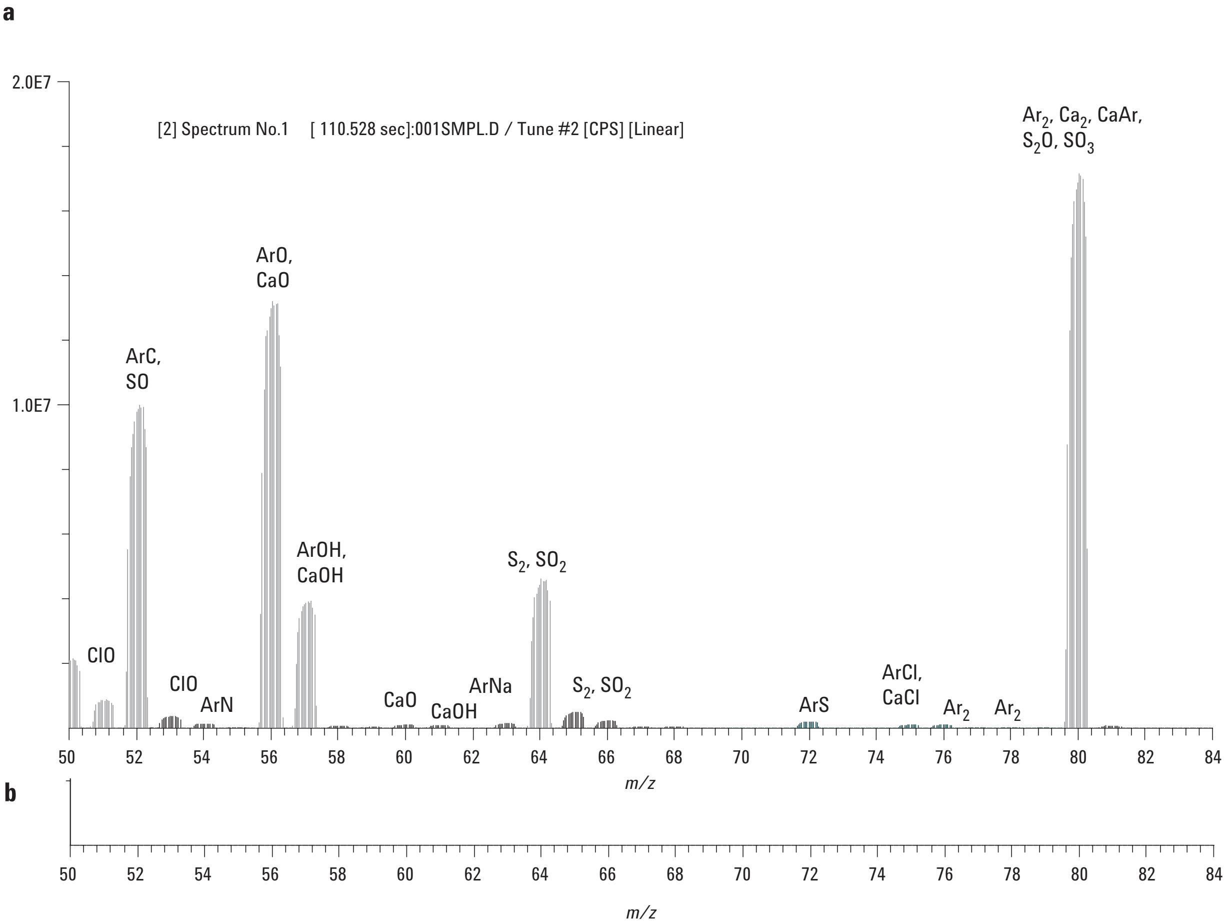

Figure 1. **High intensity interfering polyatomic ions from complex matrix sample (see text for composition) in (a) no-gas mode and (b) He collision gas mode, on same intensity scale (2.0E7).**

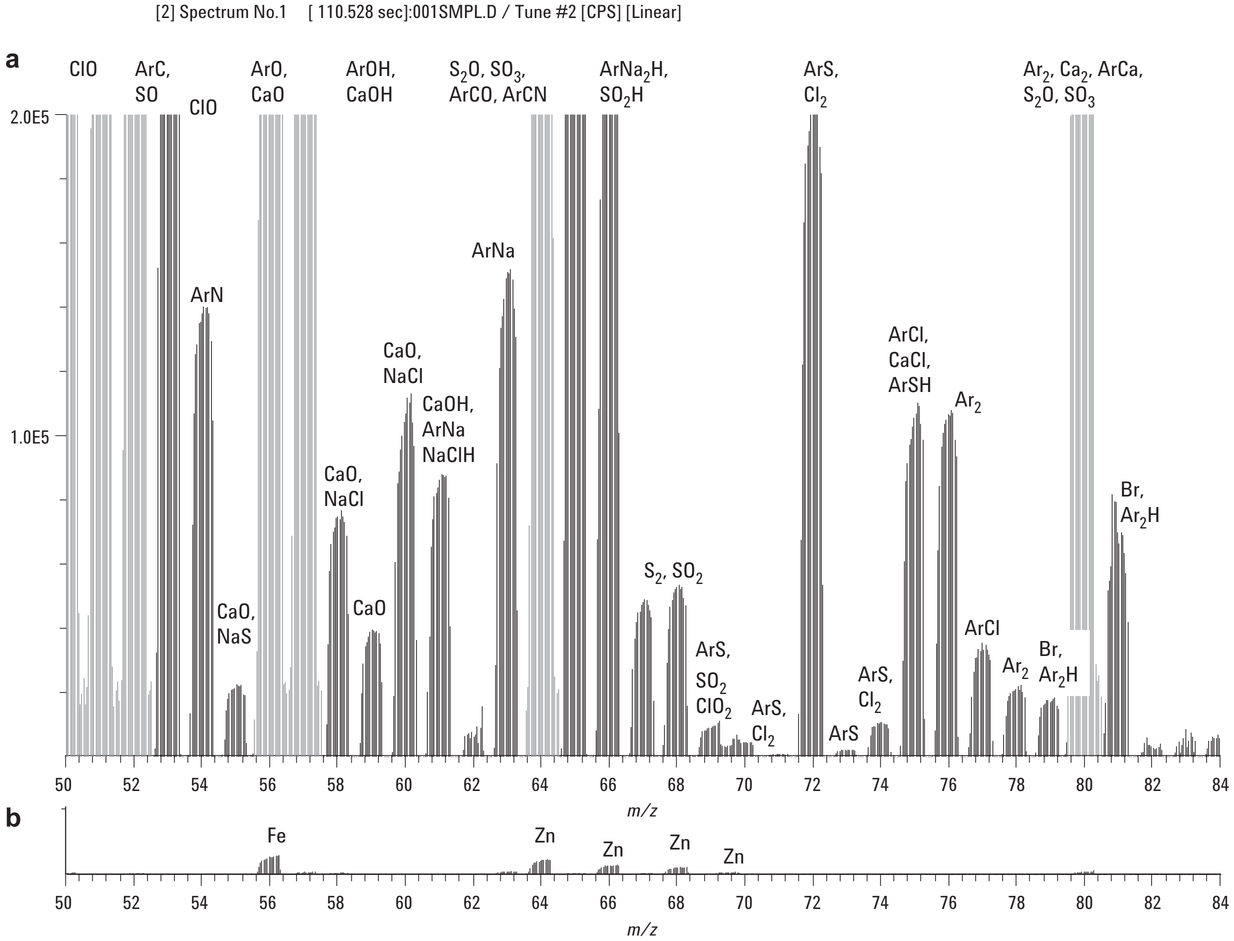

Figure 2. Low intensity interfering polyatomic ions from complex matrix sample in (a) no-gas mode and (b) He collision gas mode on same intensity scale (2.0E5), which is expanded 100x compared to Figure 1.

Measurement of Analytes in the Presence of the Sample Matrix

Having demonstrated the effective reduction of both plasma-based and matrix-based polyatomic ions using a single set of He collision mode cell conditions (Figures 1b and 2b), a second sample was analyzed. This time the sample consisted of the same multi-component matrix, but was spiked with a 5-ppb multi-element standard. Data was acquired in He collision mode to ensure that the same cell conditions used for interference removal also gave sufficient analyte sensitivity to permit the measurement of the previously interfered trace elements in this mass range. The spike consisted of 5 ppb each of V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ge, As and Se, all of which had at least one analytically useful isotope which suffered a polyatomic overlap in no-gas mode in this matrix.

Spectra obtained in He collision mode for the blank (unspiked) matrix and the spiked matrix are compared in Figures 3a and 3b respectively. Note that these spectra are shown on an intensity scale that is a further 4x lower than that used for Figures 2a and 2b, allowing the presence of the contaminant elements (Fe, Ni, Cu, Zn) to be confirmed from their isotopic templates (Figure 3b). The spectrum shown in Figure 3a clearly illustrates the capability of He collision mode to perform multi-element measurements at the low ppb level in this most complex and challenging sample matrix. Good isotopic fit is shown for every analyte. The only residual interferences observed were the plasma-based species ArOH and Ar_2 at mass 57 and 80 respectively. The Ar_2 signal at mass 80 is equivalent to ~5 µg/L Se. However, the polyatomic interferences on the other Se isotopes at *m/z* 77, 78, and 82 were removed completely, allowing Se determination at any of these isotopes (^{76}Se would also be available, but is overlapped by ^{76}Ge which was in the spike mix).

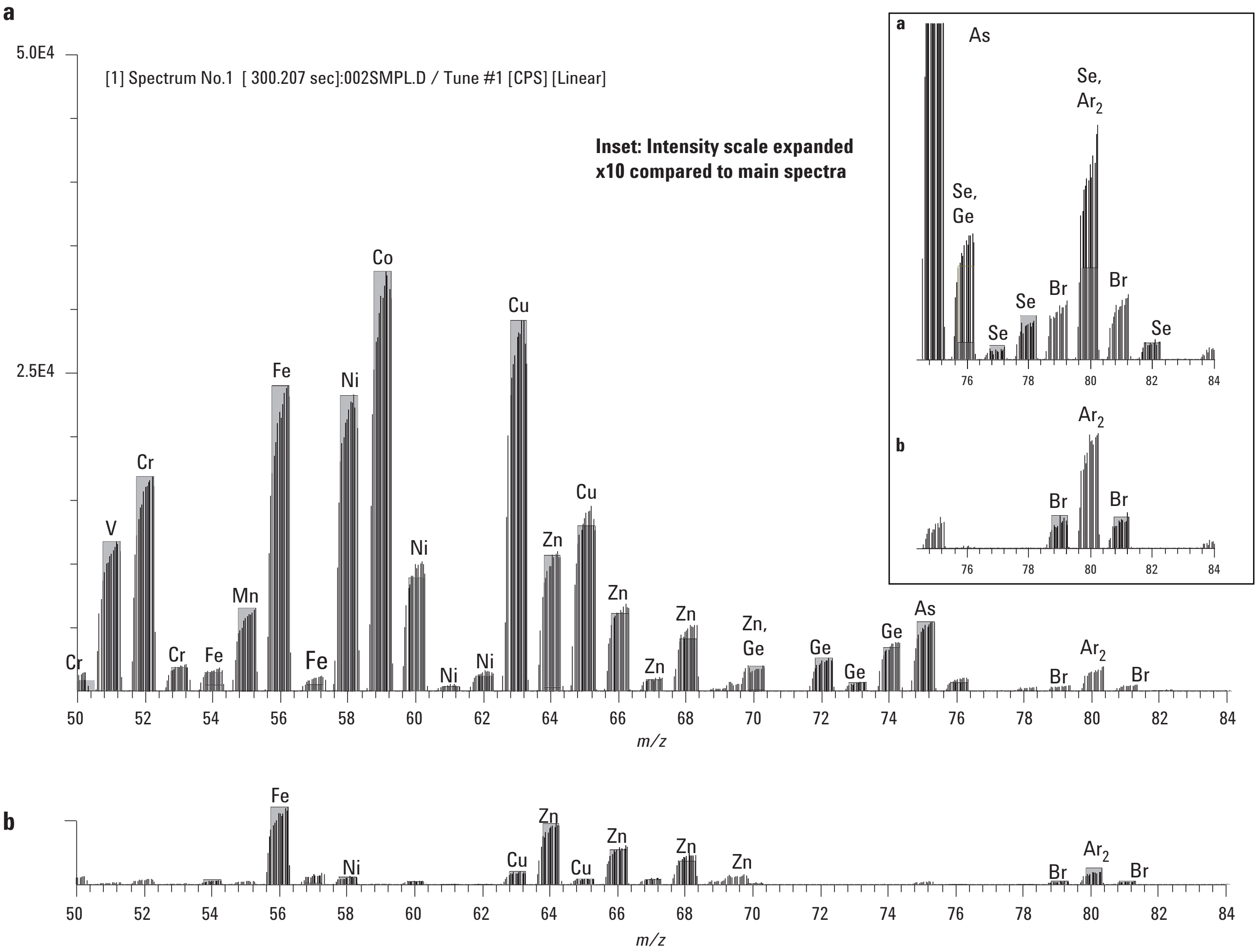

Figure 3. **Complex matrix sample in He collision mode, (a) spiked at 5 ppb with V, Cr, Fe, Mn, Ni, Co, Cu, Zn, Ge, As, and Se and (b) unspiked. Intensity scale is 5.0E4 (5.0E3 for inset spectra).**

Conclusions

The ability to remove ALL polyatomic interferences under a single set of conditions means that He mode is effectively universal – being suitable for any isotope of any element in any sample matrix. The use of He collision mode provides a unique new mode of operation, in which ALL the isotopes of each analyte become accessible. This, in turn, means that major isotopes that could not previously be used due to interferences (for example: ^{52}Cr in a carbon matrix, ^{56}Fe in any aqueous sample, ^{63}Cu in a sodium matrix, and ^{64}Zn in a sulfate matrix) - now become available. This is a great advantage to the analyst since, if desired, results can be verified by measuring many elements at both the preferred isotope AND at a second, "qualifier" isotope. Since both isotopes are free from polyatomic interference when measured using He collision mode, the use of two independent measurements gives a valuable confirmation of the reported result.

A further benefit of this powerful mode of analysis concerns sample preparation. In normal (non-CRC) ICP-MS, the choice of dilution media was limited mostly to nitric acid. Hydrochloric and sulfuric acid could not be used because of the problems of chloride or sulfur-based matrix interferences. Analysts can now choose the most appropriate digestion technique for the sample, secure in the knowledge that any new polyatomic interferences will be removed under the existing, standard He mode conditions.

The use of He collision mode on the 7500ce was demonstrated to provide effective removal of all polyatomic interferences under a single set of conditions, thereby enabling accurate multi-element analysis in complex and unknown samples. The use of an inert cell gas insures that there is no loss of analyte signal by reaction and that no new interfering species are generated, in contrast to the use of a reactive cell gas.

Since no analytes are lost by reaction and no new interferences are formed, uninterfered elements (and internal standards) can be measured under the same conditions as potentially interfered elements, and the use of a single set of cell conditions for all analytes allows multi-element analysis of transient signals (such as those derived from chromatography or laser ablation sample introduction), as well as semiquantitative screening analysis.

He collision mode is suitable for all analytes that suffer from polyatomic ion interferences and the cell conditions do not need to be set up specifically for each analyte, so the same cell conditions can be applied to new analyte suites, without requiring method development. Furthermore, since the He mode conditions are not set up specifically for the removal of individual interferences, identical cell conditions can be used for highly variable or completely unknown sample matrices, which greatly simplifies operation in a routine laboratory. The ORS enables ICP-MS to be used for the trace multi-element measurement of the most complex, real world sample matrices with no method development and with complete confidence.

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