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Advantages of reaction cell ICP-MS on doubly charged interferences for arsenic and selenium analysis in foods.~~Removal of REE doubly charged interferences on arsenic and selenium analysis in foods by ICP-QQQ~~

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Abstract

Recent reports of As concentrations in certain food and drinks has garnered public concern and led to a lowering of the US guideline maximum concentration for inorganic As in apple juice and proposed limits for As in rice products. In contrast Se is an essential micro-nutrient ~~element to human health and~~that can be limiting when Se-poor soils yield Se-poor food crops. ~~Because of its excellent detection limits, ICP-MS is commonly employed for As and Se analysis in foods. Matrix effects on As and Se analysis of foods can be severe but can be adequately corrected for by matrix matching of standards and judicious use of internal standards such as Ge and Te. Likewise, polyatomic interferences have been largely overcome through the use of collision or reaction cell technology.~~ ~~However, rear~~Rare earth element (REE) doubly charged interferences on As and Se ~~are unaffected by collision cell technology and their effect on accuracy~~ can be significant even when initial ICP-MS tuning minimizes doubly charged formation~~ at < 2%~~. We ~~illustrate this effect by analysis~~analyzed ~~of~~ NIST 1547 (peach leaves) and 1515 (apple leaves), which contain high levels of REEs, by quadrupole ICP-MS with (He) collision mode, H_2 reaction mode or triple quadrupole ICP-MS (ICP-QQQ) in mass-shift mode (O_2 and O_2/H_2). Analysis ~~of NIST 1547 and 1515~~ by ~~quadrupole~~ collision cell ICP-MS significantly over-estimated As and Se concentration due to REE doubly charged formation; mathematical correction ~~for doubly charged analytes~~ increased the accuracy of analysis but is prone to error when analyte concentration and sensitivity is low and interferent is high. ~~However, for~~For Se, H_2 reaction mode was effective in suppressing Gd^{2+} leading to accurate determination of Se in both SRMs without the need for mathematical correction. ~~Triple quad~~ ICP-QQQ~~MS~~ using mass-shift mode ~~of~~ for As^+ from m/z 75 to AsO^+ at m/z 91 and Se^+ from m/z 78 to SeO^+ at m/z 94 alleviated ~~any~~ doubly charged effects and resulted in ~~excellent recovery~~ accurate determination of As and Se ~~for~~ in both ~~NIST~~ SRMs without the need for correction equations. Zr and Mo isobars at 91 and 94 were shown to be effectively rejected by the MS/MS capability of the ICP-QQQ.

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Introduction

~~Inorganic As is a class 1 carcinogen and exposure to this element has also been linked to a host of other diseases such as cardiovascular disease and diabetes(1). Arsenic is also a naturally occurring element present in soils, surface waters and groundwater and, consequently, also in food crops.~~ The detection of As in fruit juices and in rice(1) and rice products(2) has generated much public and media interest and there are current efforts aimed at establishing regulations or guidelines for acceptable levels of As in these products, although this remains a contentious topic(3). In 2013 The US FDA proposed a new action level for inorganic As in juice of 10 μg/L(4; 5). A recent WHO document, which records the findings of the eighth meeting of the CODEX Committee on Contaminants in Food proposes a guideline for inorganic As in rice of 0.2 mg/kg(6). The proposed guideline of 0.2 mg/kg for arsenic in rice equates to a digestate concentration of 2 μg/L (assuming a 100X digestion dilution), consequently even small errors in precision and accuracy could result in a food product being classified as above the guideline when in fact it is not~~.~~ ~~Although both these guidelines require speciation analysis to determine inorganic As they will likely be preceded by a measure of total As and only if this value exceeds the regulatory limit will speciation be conducted.~~ Selenium is generally not present at elevated concentrations in most foodstuffs, ~~if fact,~~ on the contrary, Se is a micro-nutrient and some populations can be Se-deficient due primarily to Se-poor soils. Hence accurate quantification of Se in food is necessary to assess nutrient status.

~~There are several highly sensitive methods for low level measurement of As and Se including hydride generation atomic fluorescence or atomic absorption spectrometry, graphite furnace atomic absorption spectrometry and inductively coupled plasma mass spectrometry (ICP-MS)(8; 9). In this paper we focus on As and Se analysis by ICP-MS; this is now a mature, perhaps almost routine, technique. As with all analytical techniques there are potential interferences that can confound accurate and precise measurement. These interferences can by grouped into non-spectral and spectral effects in so much as they effect a general increase or decrease in analyte sensitivity or are a direct interference at m/z 75 or m/z 78 and 80. In many respects correcting for these interferences are the cornerstone of ICP-MS technology, they are well established and well described in textbooks and other research studies. However, As and Se are particularly sensitive to matrix effects and food is a particularly challenging matrix for ICP-MS. The proposed guideline of 0.2 mg/kg for arsenic in rice equates to a digestate concentration of 2 μg/L (assuming a 100X digestion dilution), consequently even small errors in precision and accuracy could result in a food product being classified as above the guideline when in fact it is not.~~

~~The large increases in As and Se sensitivity that are observed in the presence of low molecular weight organics have been reported elsewhere(10-12) and can be corrected for with a combination of matrix matching of standards, optimum internal standard selection (Ge or Te) and method of standard additions.~~ In this paper we focus on doubly charged interference from the rare earth elements (REEs) Nd, Sm and Gd, which cause 'false positives' at m/z 75 and 78 (7). The REEs have a relatively low 2nd ionization potential ca. 11 – 12 eV and some doubly charged formation is inevitable in an Ar plasma. ~~Doubly charged formation~~This is a particular problem for As and Se ~~analysis~~ when the analytes are present at low concentration in the sample compared to the REEs and the effect is exacerbated by the fact that both As and Se are relatively poorly ionized in the plasma, hence, the sensitivity or slope of their calibration is low and false signals at either mass can equate to significant concentration errors. Both Nd and Sm REE have isotopes at 150 amu, where Sm is 7.4% abundant and Nd is 5.6% abundant, while Gd is 20.5% abundant at m/z 156 (Dy is also 0.06% abundant at this mass). ~~Although the group name for the lanthanides implies they are rare, they are actually of greater crustal abundance than either As or Se.~~ Because REEs are immobile in soils, certain soils can be relatively enriched in REEs and consequently food crops grown on these soils may take up higher concentrations of these elements~~ (12; 13)~~(8; 9). Two NIST standard reference materials, NIST 1515 apple leaves and NIST 1547 peach leaves, that are useful for quality control in food and plant analysis contain low µ~~n~~g k~~/~~g^{-1} levels of As and Se in the presence of ~~µg~~mg~~/~~ kg^{-1} levels of REEs. Quantification of As and Se in these two reference materials is confounded by doubly charged interference of the REEs at m/z 75 and 78. ~~In theory, doubly charged interferences are well-understood, all ICP-MS tuning will attempt to minimize their formation to 2% or less. However, even at 1 % doubly charged formation, measured by analyzing Ce^{2+}/Ce^{+} (m/z 70/140), the levels of REEs in some food or juice products could be sufficient to lead to a significant over-estimation of As and Se concentration.~~ While some standard methods recommend monitoring masses at 150 and correcting for doubly charged ions through the use of mathematical equations, it is debatable how widespread this procedure is followed and in any event, correction equations are less accurate than quantification at m/z that is free from any interference. We illustrate the doubly charged effect by analysis of NIST apple leaves and peach leaves and test the effectiveness of interference correction equations, KED (He only) and H_2 reaction cell ICP-MS and 'mass shifting' by use of O_2 and O_2/H_2 as a reaction gas using ICP-QQQ. ~~We used the~~ The ~~new 'triple quad' design (~~ICP-QQQ~~)~~ ~~which~~ uses a quadrupole mass filter before (Q1) and after (Q3) the reaction cell. The unit mass resolution of the first quadrupole selectively allows for only a single m/z (eg. mass 78) to enter the collision reaction cell. Thus, except for the analyte and those interferences at the selected mass, no other analyte or polyatomic molecules enter the cell ~~ensuring~~ allowing targeted and selected chemical reaction to take place.

Materials and methods

All samples were acid digested using a MARS6 (CEM, Mathews, NC) closed vessel digestion at 200 °C with a 20 minute ramp and 20 minute hold time. Triplicate samples of NIST (US National Institute of Standards and Technology, Gaithersburg, MD) SRMs 1547 (peach leaves), 1515 (apple leaves) were digested using 0.25g sample 2.5 mls 9:1 HNO_3:HCl and diluted to a final digested weight of 25g. NIST 1547 and 1515 contain low µg kg concentrations of As and Se (Table 1) and high concentrations of REEs. NIST 1547 certification gives reference (non-certified) values for Nd, Sm and Gd concentrations at 7, 1, and 1 mg kg^{-1} and NIST 1515 has reference values for Nd, Sm and Gd concentrations at 17, 3, and 3 mg kg^{-1}, respectively. Samples were run at Dartmouth College by collision cell ICP-MS (Agilent 7700x) using He as the collision gas at 4.5 ml/min and H_2 as reaction gas at 6 ml/min and at Agilent Technologies (Wilmington, Delaware) by ICP-QQQ (8800) using O_2 ~~-~~or O_2/H_2 as reaction gas at 3.5 ml/min with AsO^+ detection at m/z 91 and SeO^+ detection at m/z 94 and 96. ~~For b~~Both instrument set-ups used manufacturer-recommended operating conditions and utilized a concentric nebulizer and Peltier cooled double pass spray chamber, ~~internal~~ internal standard was added online. ~~into the sample stream via the~~

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~~second position on the peristaltic pump.~~ The Dartmouth system is operated with 5% butanol in the internal standard mixture to equalize the organic plasma load between samples and standards and was calibrated using both external calibration and standard additions; the standard additions data gave more accurate data for both SRMs and is reported here. ~~–~~ ~~The Dartmouth 7700X was operated with a CETAC express system to increase sample throughput.~~ Both instruments were calibrated using NIST- traceable standards and ~~used~~ traceable 2nd-source calibration checks. ~~-~~The measured values were considered not significantly different than the certified values if their 95% confidence interval overlapped with the 95 % confidence range reported on the NIST certificate.

Results and Discussion

Both kinetic energy discrimination (KED, collision cell technology) ~~or~~ and reactive gases have been used to reduce polyatomic interferences in ICP-MS but their effect, if any, on doubly charged formation is less often reported. ~~For As analysis it is necessary to minimize polyatomic interferences at m/z 75 most usually arising from ArCl and CaCl, while for Se analysis the two major analytes (m/z 78 and 80) are overlapped by Ar dimers.~~ The effect of collision (He) and reaction (H_2) gases on polyatomic interferents, analyte signal and doubly charged formation at m/z 75 and 78 are shown in figure 1. Both He and H_2 effectively reduce polyatomic interferences; however analyte intensity is also reduced as cell gas flow rate is increased. Helium gas flow rate has no effect on reducing doubly charged interference from Sm or Nd at m/z 75 (Figure 1A) or from Gd at m/z 78 (Figure 1C), in fact apparent doubly charged formation increases as He gas flow increases, presumably because KED reduces the singly-charged ion intensity relatively more than the doubly charged ion, which may be due to the difference is size between these two differently charged ions. ~~Ignoring doubly charged ions, t~~The optimum He flow for reducing polyatomics and maintaining high signal to noise is 4.5 ml/min. Hydrogen is very effective as a reaction gas in reducing Ar-based interferences, with optimal signal to noise ratio obtained at flow rates ca. 3- 4 ml/min (Figure 1D), however, doubly charged formation for Gd (Figure 1D) and Nd and Sm (Figure 1B) remain high at this gas flow rate. Increasing the H_2 flow rate to 5.5 – 6 ml/min effectively removes Gd doubly charged interference while still maintain good signal to noise ratio for Se. Similarly Nd and Sm doubly charged formation is dramatically reduced at this higher flow rate to 0.03 and 0.01 % respectively, at the expense, however, of severe reduction in As intensity and signal to noise ratio. ~~Based on these results one would predict that neither collision cell ICP-MS or reaction cell with H_2 as the reaction gas would be effective for low level As measurements in the presence of REEs, while H_2 reaction cell ICP-MS at flow rates of 6 ml/min could be effective for Se analysis.~~

Using the method development criteria determined above, NIST SRMs 1515 and 1647 were determined in both He and H_2 gas modes with KED. ~~Helium flow rate was 4.5 ml/min and H_2 was 6 ml/min, integration times were 1 second for both As and Se.~~ Doubly charged ion formation was 1.1%, 0.9% and 0.25% for Nd, Sm and Gd in He-mode and 0.06%, 0.036% and 0.006% for H_2 mode. The trend of decreasing doubly charged formation with increasing REE atomic weight reflects the increase in 2nd ionization potential across the period. Hydrogen is clearly effective in reducing doubly charged interferences in the cell. Approximate instrument detection limits derived from the calibration statistics and used here for comparative purposes were 0.01 µg/L and 0.06 µg/L for As and Se respectively in KED (He) mode and 0.022 µg/L and 0.03 µg/L in H_2 mode. The instrument sensitivity for each analyte in each

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mode, as indicated by the calibration slope, was 1.52 and 0.076 for As in He and H_2 mode respectively and 0.15 and 0.25 for Se in He and H_2 mode respectively.

The results for As and Se determination of NIST 1515 and 1547 by collision cell ICP-MS are shown in Table 1. ~~NIST 1547 are certified for As at 0.06 mg/kg and contain Nd and Sm at 7 and 1 mg/kg, respectively. Consequently with a 100-fold digestion dilution the resulting solution for analysis contains 600 ng/L As and 70 and 10 µg/L Nd and Sm respectively. Quantitative analysis of NIST 1515 is even more challenging for As due to lower As and higher REE concentrations. The certified As value is 0.038 mg/kg while reference Nd and Sm values are 17 and 3 mg/kg, respectively. Clearly, a~~Accurate analysis of As in either He or H_2 mode for either SRM material was not obtained if doubly charged ions were not accounted for~~. Because He mode does not attenuate doubly charged ion formation it is not surprising that the calculated concentration of As was over-estimated for both SRMs and that apple leaves, with lower As and higher interferent, was over-estimated to a greater extent.~~ The uncorrected As value of 0.25 mg/kg for NIST 1515 is above the proposed 0.2 mg/kg guideline for inorganic As in rice, illustrating that doubly charged interferences can cause large false positives that could potentially lead to unnecessary further analysis for inorganic As content. Uncorrected As values in reaction mode are ~~much~~ less than for He mode but still overestimate the certified values by 1.9 and 3.3 times for NIST 1547 and 1515, respectively~~. Clearly doubly charged formation at m/z 75 is suppressed in H_2 reaction mode but the~~ as residual doubly charged formation and low sensitivity for As at this H_2 flow rate ~~still~~ lead to significant positive bias.

~~Before the advent of collision and reaction cell technology, mathematical correction equations were commonly used to correct for interferences. It is possible to correct for doubly charged formation by multiplying the average % doubly charged formation observed for Nd and Sm to the counts recorded at m/z 150 in the sample and subtracting this from the counts at 75.~~ Mathematical correction of doubly charged species for As resulted in a value of 0.068 mg/kg for NIST 1547, ~~a 60% reduction in the uncorrected value and now~~ within the confidence interval of the certified value. Corrected values for NIST 1515 were ~~90% less than the uncorrected value and much closer to the certified value. In this instance the corrected value was 68% of the certified value and below~~ also not significantly different than the certified range. However, this was largely due to the high~~.~~ ~~The~~ RSD of the measured ~~corrected~~ replicate values, ~~for NIST 1515 was 42%~~ which illustrates a problem of correction equations when the signal is mostly interferent as opposed to analyte. ~~Similarly, c~~Corrected values for As in H_2-reaction mode ~~are lower than the uncorrected values and closer to the certified values. However, both measured values~~were not significantly different that the certified values but were at the positive extreme of each SRM confidence interval ~~are outside the confidence range of the certified material~~ with recoveries of 132% and 124% for NIST 1547 and 1515, respectively.

~~The situation for Se in He mode is essentially the same as for As described above; low~~ Low Se sensitivity in He mode and high Gd in both SRMs (3 mg/kg and 1 mg/kg for NIST 1515 and 1547 respectively) ~~lead~~ caused~~to very~~ large over-estimates of the true Se values when uncorrected. Using correction equations for NIST 1547 gives a value of 0.113 mg/kg which is within the certified confidence range. The corrected value for Se in He mode in NIST 1515 is 0.013 mg/kg~~, significantly below the certified value~~ and had an unacceptably high CV (150%), ~~and~~ again demonstrat~~es~~ing the problems of correction equations when

Journal of Analytical Atomic Spectrometry Accepted Manuscript

the signal is essentially 95% doubly charged interference. In H_2 reaction mode the high sensitivity for Se and removal of doubly charged interferences at m/z 78 ~~mean that quantitative data for both NIST SRMs are obtained~~resulted in accurate values for both SRMs that were not significantly difference than the certified values. Detection limits for Se in H_2 mode are better than for He mode and doubly charged formation is reduced to 0.006% such that accurate and precise Se data are obtained~~ with recoveries of 99% and 98% obtained for NIST 1547 and 1515 respectively~~. This effect has also been reported in a recent study where it was shown that H_2 can eliminate double charge interference for Se in the presence of Gd in blood of patients receiving MRI Gd-based contrasting agents(10).

The pitfalls of mathematical corrections and the general poorer results for As in either He or H_2 modes described above led us to investigate other reaction gases. Reaction gas ICP-MS methods(11) have been used successfully for As and Se with gases such as NH_3 (14), CH_4 (7; 12-15)), and O_2 (13; 16) although these studies mostly focused on polyatomic interference removal rather than doubly charged interferences. Reaction with O_2 mass shifts As and Se analytes to m/z 91 and 94 (or 96) where background is generally lower and the new m/z less prone to interferences, provided isobars from Zr and Mo at the mass shifted m/z are filtered away from the reaction cell and polyatomic interferences at the new m/z are not created in the cell. ~~We used the new 'triple quad' design (ICP-QQQ) which uses a quadrupole mass filter before (Q1) and after (Q3) the reaction cell. The unit mass resolution of the first quadrupole selectively allows for only a single m/z (eg. mass 78) to enter the collision reaction cell. Thus, except the analyte and those interferences at the selected mass, no other analyte or polyatomic molecules enter the cell ensuring targeted and selected chemical reaction to take place.~~ We ran both NIST SRM digests by reaction cell ICP-QQQ using either O_2 or O_2/H_2 as the reaction gas. The O_2/H_2 mixture was included because previous work has shown that the extent of the Se reaction with O_2 is enhanced in the presence of H_2. The H_2 gas reduces Ar-dimer interferences~~, which as isobars of the two Se isotopes were allowed to enter the cell by the first quadrupole,~~ facilitating an increased reaction rate between Se and O_2. Table 2 gives the instrument response at each of the mass shifted analyte m/z for the calibration blank and 50 and 100 µg/L solutions of Nd/Dy and Gd/Sm. The slope of the calibration curve and the detection limit, estimated from the standard deviation of 3 independent blank measurements during the run ~~is~~are also shown in Table 2. There is no systematic increase in background signal resulting from 50 or 100 ppb solutions of REEs at the mass shifted analyte masses in either gas mode. In this mass shifted mode it is possible to measure Se 80 isotope which being the most abundant isotope should give lower detection limits. However, Se 78 has slightly lower background signals at the mass shifted m/z and gives slightly lower detection limits of 0.002 µg/l compared to 0.003 µg/l ^{80}SeO, however also note that these are 10 times lower than detection limits for Se by H_2-reaction mode by conventional reaction cell on a single quadrupole ICP-MS. For both ^{78}Se and ^{80}Se the calibration slope increases two fold in O_2/H_2 mode compared to O_2 reaction mode indicating increased SeO formation; and for ^{80}Se the background is also significantly lower. Clearly, for Se, there is advantage in using the mixed gas rather than just O_2. There is no effect of reaction gas on sensitivity or detection limit for As so either approach is suitable and gives essentially the same results. Detection limits for As are ca. 0.001 µg/l, 10 times lower than for collision cell ICP-MS.

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The results for analysis of the NIST 1515 and 1547 using the ICP-QQQ approach are shown in Table ~~3~~1. For As in NIST 1515 and 1547 the measured values were 0.032 and 0.065 respectively, both well within the respective certified confidence range for the SRM. Similarly, recoveries for Se are excellent, both being within the certified range for NIST 1515 and 1547. Hence doubly charged interference from the high REE levels of these two SRMs is eliminated through this O_2/H_2 reaction mode approach. Zirconium and Mo have isotopes at m/z 91 and 94 but should be rejected by the first quadrupole filter prior to entering the cell. To test this, an aliquot of NIST 1547 was spiked at 1 mg/L Zr and Mo and the results are also shown in Table ~~3~~1. The measured values for As and Se are not different than the unspiked samples proving that the MS/MS capability is effective at rejecting isobars of similar mass to the new mass-shifted analyte.

Conclusions

~~While all analytical techniques are subject to some degree of interference, the analysis of As and Se in foods by ICP-MS is particularly challenging because of matrix-induced sensitivity effects and potential doubly charged formation and the relatively low analyte concentration.~~ Doubly charged formation is best addressed by reaction cell based approaches as collision cell ICP-MS is not effective at removing doubly charged species and correction equations are prone to error. Either H_2 to remove the doubly charged species or O_2/H_2 to mass shift Se at m/z 94 are effective for Se analysis. For As, using O_2 to mass shift to AsO at m/z 91 was the most effective approach. ICP-QQQ also had 10-fold lower detection limits than the single quadrupole ICP-MS, which makes it particularly suited to low level determination of As and Se in complex sample matrices. ~~The extent of the doubly charged formation depends on the presence of Sm, Nd and Gd in the sample.~~ The extent and concentrations of REEs in food products is not well studied but their occurrence in two NIST reference materials suggests REEs can be expected in some foods depending on soil concentrations during crop production. ~~Arsenic concentration can be significantly over-estimated in the presence of uncorrected doubly charged formation, to such an extent that it could cause a food product to be classified as over a guidance limit for As when in fact it is not.~~ At a minimum, m/z 150 and 156 should be monitored during any analysis to flag samples where doubly charged formation could be problematic, but reaction cell approaches in general and ICP-QQQ approaches in particular are most appropriate in making accurate low level analyses.

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~~Table 1: Analysis of As and Se (m/z 78) in NIST 1547 and 1515 in KED and reaction modes uncorrected and corrected for doubly charged interference.~~

		~~Arsenic~~			
		~~KED-He~~		~~reaction-H_2~~	
	~~ceritifed~~	~~uncorrected~~	~~corrected~~	~~uncorrected~~	~~corrected~~
~~Peach~~	~~0.060 ± 0.018~~	~~0.170 ± 0.009~~	~~0.068 ± 0.002~~	~~0.113 ± 0.002~~	~~0.079 ± 0.002~~
~~Apple~~	~~0.038 ± 0.007~~	~~0.250 ± 0.009~~	~~0.026 ± 0.011~~	~~0.126 ± 0.003~~	~~0.047 ± 0.002~~
		~~Selenium~~			
~~Peach~~	~~0.120 ± 0.009~~	~~0.394 ± 0.02~~	~~0.113 ± 0.02~~	~~0.119 ± 0.005~~	~~0.119 ± 0.005~~
~~Apple~~	~~0.050 ± 0.009~~	~~0.808 ± 0.02~~	~~0.013 ± 0.02~~	~~0.050 ± 0.002~~	~~0.050 ± 0.002~~

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~~Table 2: ICP-MS response at mass shifted m/z for As and Se in the presence of REEs and sensitivity and estimated detection limits for As and Se at these m/z by ICP-QQQ.~~

	~~75 -> 91 As~~		~~78 -> 94 Se~~		~~80 -> 96 Se~~	
	~~[O_2]~~	~~[O_2/H_2]~~	~~[O_2]~~	~~[O_2/H_2]~~	~~[O_2]~~	~~[O_2/H_2]~~
~~Blank (cps)~~	~~6.00~~	~~36.00~~	~~0.00~~	~~2.00~~	~~27.33~~	~~6.00~~
~~50 ppb Nd/Dy (cps)~~	~~22.67~~	~~43.33~~	~~0.67~~	~~0.00~~	~~25.33~~	~~7.33~~
~~100 ppb Nd/Dy (cps)~~	~~8.00~~	~~19.33~~	~~0.00~~	~~0.00~~	~~22.67~~	~~2.67~~
~~50 ppb Gd/Sm (cps)~~	~~17.33~~	~~44.00~~	~~2.00~~	~~3.33~~	~~20.00~~	~~6.67~~
~~100 ppb Gd/Sm (cps)~~	~~16.00~~	~~76.67~~	~~4.00~~	~~4.00~~	~~20.00~~	~~6.00~~
~~slope (cps/ng l^{-1})~~	~~6.40~~	~~6.33~~	~~0.26~~	~~0.53~~	~~0.60~~	~~1.30~~
~~estimated detection limit (µg/l)~~	~~0.0010~~	~~0.0013~~	~~0.0090~~	~~0.0022~~	~~0.0135~~	~~0.0032~~

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~~Table 3: Certified and measured As and Se concentrations in NIST 1515 and 1547 by ICP-QQQ~~

	~~75 -> 91 As [O_2/H_2]~~		~~78 -> 94 Se [O_2/H_2]~~	
	~~Certified~~	~~measured~~	~~Certified~~	~~measured~~
~~NIST 1515, Apple leaves~~	~~0.038 ± 0.007~~	~~0.032± 0.001~~	~~0.050 ± 0.009~~	~~0.047± 0.003~~
~~NIST 1547, Peach Leaves~~	~~0.060 ± 0.018~~	~~0.065 ± 0.001~~	~~0.120 ± 0.009~~	~~0.127± 0.003~~
~~NIST 1547: Spiked at 1 mg/L Zr and Mo~~		~~0.063~~		~~0.130~~

Arsenic (mg kg^{-1})						
-		KED-He		reaction-H_2		ICP-QQQ reaction-O_2/H_2
SRM	certified	uncorrected	corrected	uncorrected	corrected	uncorrected
NIST 1547	0.060 ± 0.018	0.170 ± 0.016	0.068 ± 0.003	0.113 ± 0.004	0.079 ± 0.004*	0.065 ± 0.002*
NIST 1515	0.038 ± 0.007	0.250 ± 0.016	0.026 ± 0.021	0.126 ± 0.005	0.047 ± 0.004*	0.032± 0.002*
				NIST 1547 spiked at 1 mg l^{-1} Zr and Mo (n=1)		0.063
Selenium (mg kg^{-1})						
-		KED-He		reaction-H_2		ICP-QQQ reaction-O_2/H_2
SRM	certified	uncorrected	corrected	uncorrected	corrected	uncorrected
NIST 1547	0.120 ± 0.009	0.394 ± 0.04	0.113 ± 0.02*	0.119 ± 0.009*	0.119 ± 0.009*	0.127± 0.006*
NIST 1515	0.050 ± 0.009	0.808 ± 0.04	0.013 ± 0.04*	0.050 ± 0.003*	0.050 ± 0.003*	0.047± 0.006*
				NIST 1547 spiked at 1 mg l^{-1} Zr and Mo (n=1)		0.13

Table 1: Analysis of As and Se (m/z 78) in NIST 1547 and 1515 in KED and reaction modes uncorrected and corrected for doubly charged interference and by ICP-QQQ. All concentrations are in mg/kg, and are averages of 3 replicate sample digests expressed as mean ± 95% confidence interval. Means marked * have 95% confidence intervals that overlap with the certified range.

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Table 2: ICP-MS response at mass shifted m/z for As and Se in the presence of REEs and sensitivity and estimated detection limits for As and Se at these m/z by ICP-QQQ.

	75 -> 91 As		78 -> 94 Se		80 -> 96 Se	
	[O_2]	[O_2/H_2]	[O_2]	[O_2/H_2]	[O_2]	[O_2/H_2]
Blank (cps)	6.00	36.00	0.00	2.00	27.33	6.00
50 ppb Nd/Dy (cps)	22.67	43.33	0.67	0.00	25.33	7.33
100 ppb Nd/Dy (cps)	8.00	19.33	0.00	0.00	22.67	2.67
50 ppb Gd/Sm (cps)	17.33	44.00	2.00	3.33	20.00	6.67
100 ppb Gd/Sm (cps)	16.00	76.67	4.00	4.00	20.00	6.00
slope (cps/ng l^{-1})	6.40	6.33	0.26	0.53	0.60	1.30
estimated detection limit (µg l^{-1})	0.0010	0.0013	0.0090	0.0022	0.0135	0.0032

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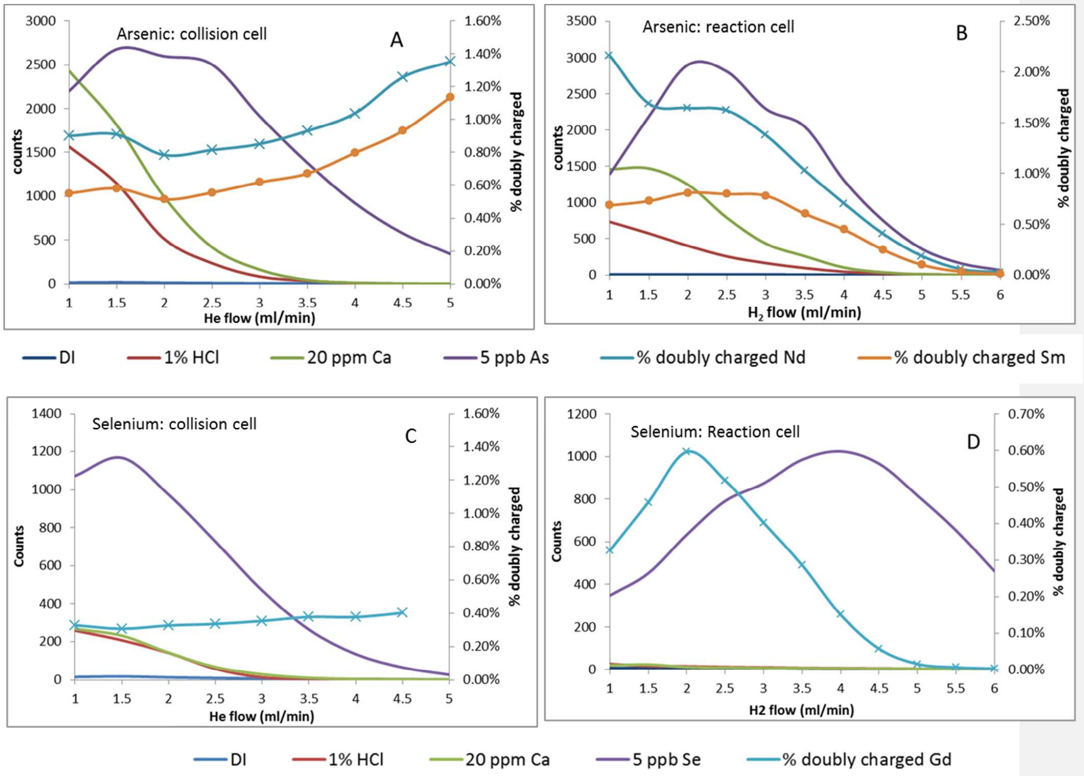
Figure 1: Analyte, polyatomic and doubly charged instrument response at m/z 75 (A, B) and m/z 78 (C,D) as a function of collision (A,C) or reaction (B.D) gas flow rate in a single quadrupole ICP-MS.



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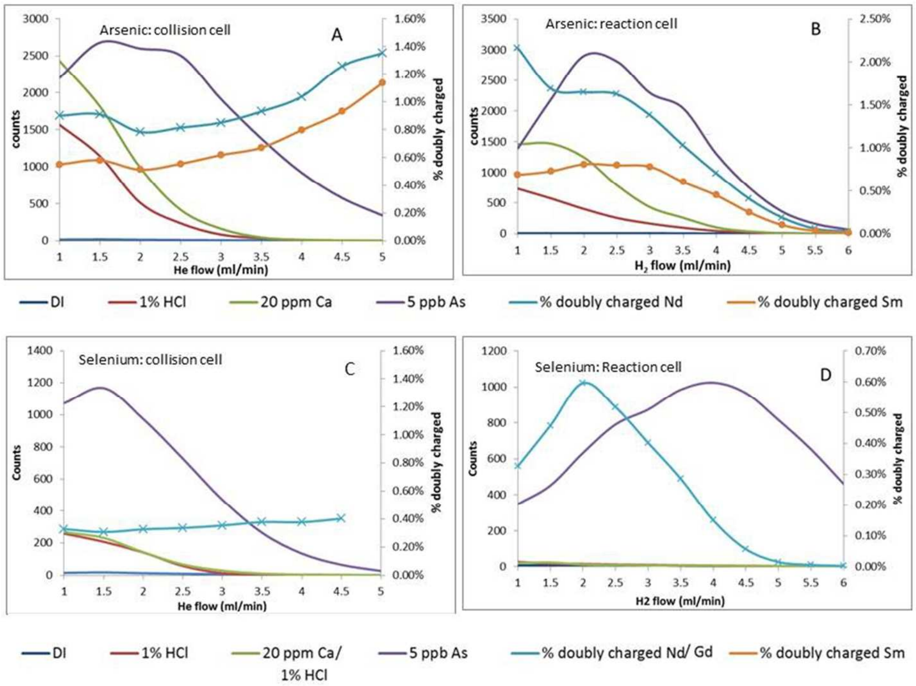

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